Carbon–Hydrogen Bond Activation by Peralkylhafnocene and Peralkylscandocene Derivatives

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Chapter 1

Intramolecular C–H Bond Activation of Benzyl Ligands by Metallated–Cyclopentadienyl Derivatives of Permethylhafnocene. Molecular Structure of $(\eta^5\text{-}C_5Me_5)(\eta^5,\eta^1\text{-}C_5Me_4CH_2)HfCH_2C_6H_5$ and the Mechanism of Rearrangement to Its Hafnabenzocyclobutene Tautomer $(\eta^5\text{-}C_5Me_5)_2\overline{HfCH_2\text{-}o\text{-}C}_6H_4$.

Abstract: Thermal decomposition of $Cp^*_2Hf(CH_2C_6H_5)_2$ ($Cp^* = (\eta^5\text{–}C_5Me_5)$) in benzene–$d_6$ cleanly affords toluene and hafnabenzocyclobutene $Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$. Deuterium labeling of the benzyl ligands indicates that decomposition of $Cp^*_2Hf(CY_2C_6H_5)_2$ (Y = H, D) proceeds primarily by α–H abstraction to form a permethylhafnocene benzylidene intermediate $[Cp^*_2Hf{=}CHC_6H_5]$, which rapidly rearranges to the metallated–cyclopentadienyl, or "tucked–in" benzyl complex $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$. The observed product arises from rearrangement of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$ to its tautomer $Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$. A series of *meta* substituted benzyl derivatives of the proposed metallated cyclopentadienyl intermediates, $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_4X$ (X = H, CH_3, CF_3, NMe_2), has therefore been prepared. The kinetics of their conversion to $Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_3X$ have been examined in order to probe the nature of the transition state for aryl C–H bond activation which occurs in the final steps of the rearrangement. The rates are found to be insensitive to the nature of X, suggesting that the benzyl π system is *not* attacked by the electrophilic hafnium center along the reaction coordinate for C–H bond activation. The structure of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$, as determined by single crystal X–ray diffraction techniques, indicates that the complex is best described as a Hf(IV) derivative containing an $\eta^5,\eta^1\text{–}C_5Me_4CH_2$ ligand, rather than a Hf(II) η^6–fulvene adduct. $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$ crystallizes in the triclinic space group $P\bar{1}$ ($a = 9.084(2)$, $b = 10.492(2)$, $c = 12.328(1)$ Å; $\alpha = 95.81(1)$, $\beta = 96.60(1)$, $\gamma = 91.15(2)$; $Z = 2$). Least–squares refinement led to a value for R of 0.048 ($I > 3\sigma I$) and a goodness–of–fit of 4.37 for 4029 independent reflections.

Introduction

High valent, early transition metal, lanthanide and actinide complexes have been shown to be reactive towards both aromatic and aliphatic carbon–hydrogen bonds.[1] Associative mechanisms proceeding through highly ordered, polar, 4–centered transition states typically have been invoked for C–H bond cleavage by these d^0 (or d^0f^n) metal systems.[2] An electrophilic aromatic substitution in which the metal interacts initially with the arene π system represents an alternative mechanism for aromatic C–H bond activation.[3] This type of mechanism seems particularly feasible in view of the electron deficient, highly Lewis–acidic nature of coordinatively unsaturated d^0 metal centers. *Trihapto* coordination of the benzyl ligands of $Zr(OR)(CH_2C_6H_5)_3$ (R = 2,6–di–*tert*-butylphenyl), as evidenced by the X–ray crystal structure, demonstrates such a π arene–Lewis acid interaction.[4] Similarly, the crystal structures of $Cp^*Th(CH_2C_6H_5)_3$[5] and $M(CH_2C_6H_5)_4$ (M = Ti, Zr, Hf)[6] show the metal to be interacting with the π systems of the benzyl ligands.

There are several examples of transition metal complexes serving as electrophiles in aromatic substitution reactions. Ogoshi *et al.* reported that arene C–H bond activation by a cationic Rh(III) complex occurred *via* electrophilic aromatic metallation.[7] Shul'pin and co–workers have invoked a similar mechanism for arene activation at an anionic Pt(IV) center.[8] The intramolecular cyclopalladation of ligands such as azobenzene has also been suggested to occur by electrophilic aromatic substitution, with rearrangement of a π– to σ–arene adduct, followed by loss of a proton leading to the observed aryl product.[9] Deeming and Rothwell, however, have shown that cyclopalladation can also occur with benzo[h]quinoline ligands constrained by chelation from forming a π complex.[10] Graham has prepared η^2–arene complexes of the type $[(\eta^5\text{–}C_5H_5)Re(NO)(CO)(\eta^2\text{–arene})]^+$, which closely resemble the proposed intermediates of electrophilic aromatic substitutions.[11]

Jones and Feher have developed a convincing case for the intermediacy of a π–arene adduct along the reaction coordinate leading to C–H bond addition to coordinatively unsaturated $[Cp^*Rh(PMe_3)]$[12], although this electron–rich rhodium center is not likely to be a strong Lewis acid.

In order to probe the mechanism by which electron deficient, d^0 metal complexes activate aromatic carbon–hydrogen bonds we have examined the thermal decomposition of a series of *bis*(benzyl) derivatives of permethylhafnocene, $Cp^*_2Hf(CH_2C_6H_4\text{–}m\text{–}X)_2$ (Cp^* = η^5–C_5Me_5; X = H, CH_3, NMe_2), which cleanly afford toluene (or the substituted toluene) and the hafnobenzocyclobutene complexes $Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_3X$. Although the most straightforward decomposition pathway to the observed products is direct *ortho* C–H abstraction from a benzyl ligand by the other $Hf\text{–}CH_2C_6H_5$ group, a close examination revealed that the mechanism is much more complex; both benzylidene and metallated cyclopentadienyl intermediates are involved. We report herein the synthesis, reactivity and X–ray structure determination of one intermediate, $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$, and the results of a study of the mechanism of its rearrangement to $Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$.

Results and Discussion

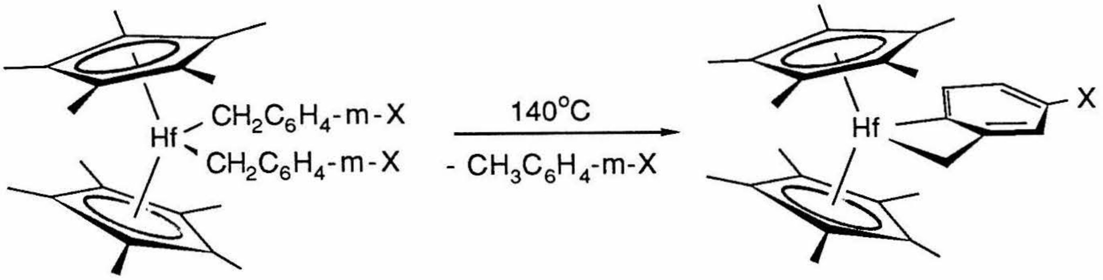
Permethylhafnocene dichloride, $Cp^*_2HfCl_2$ (**1**), reacts rapidly in benzene solution with two equivalents of the appropriate benzyl potassium reagent[13] to give the dibenzyl complexes **2–4** (equation 1).

$$\underset{\mathbf{1}}{Cp^*_2HfCl_2} + 2\ K(CH_2C_6H_4\text{–}m\text{–}X) \longrightarrow Cp^*_2Hf(CH_2C_6H_4\text{–}m\text{–}X)_2 + 2\ KCl \qquad (1)$$

2, X = H
3, X = CH_3
4, X = NMe_2

Isolation from petroleum ether affords **2–4** in good yields as pale yellow crystalline compounds, which may be handled briefly in air and are indefinitely stable at room temperature under an N_2 atmosphere.

Thermolysis of benzene or toluene solutions of **2–4** yields the hafnabenzocyclobutenes **5–7** and *meta*–substituted toluene (equation 2).[14]



(2)

2-4

5, X = H
6, X = CH_3
7, X = NMe_2

The conversion of complexes **2–4** to metallacycles **5–7** and toluene follows first order kinetics for 2–3 half–lives.

Abstraction of an *ortho*–benzyl hydrogen by the neighboring Hf–benzyl group is the most direct mechanism for the thermal decomposition of **2** to **5**. Hence, we undertook an investigation of the relative rates of decomposition of the *meta*-substituted dibenzyl complexes **5-7** in order to distinguish between an electrophilic aromatic substitution–like mechanism, proceeding through an η^1–phenonium ion intermediate or transition state[15], and a mechanism in which the arene C–H σ bond and Hf–benzyl bonds undergo sigma bond metathesis without interaction of the hafnium center with the arene π system.

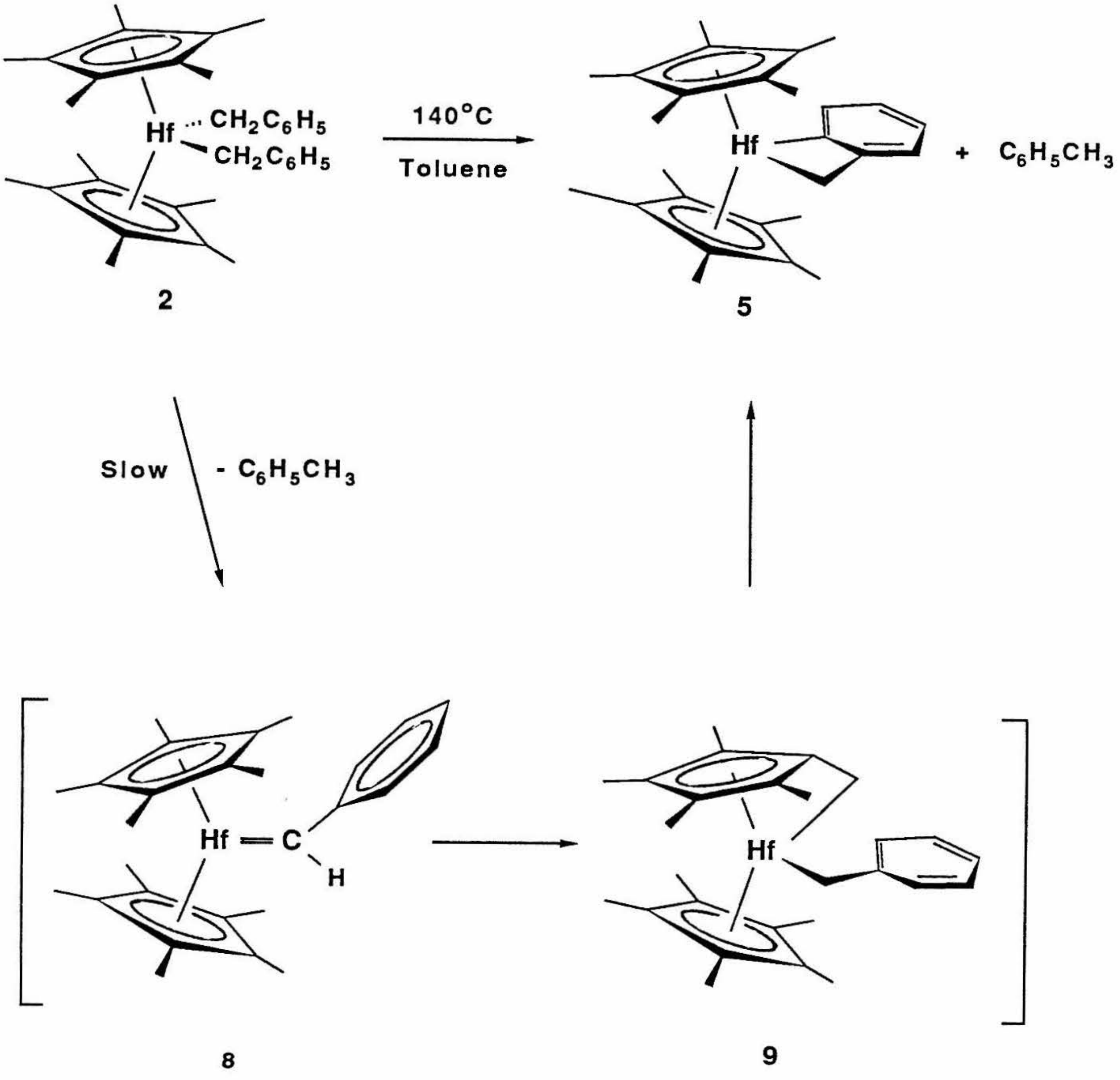
To probe whether this straightforward mechanism is, in fact, being followed, the isotopically labeled dibenzyl complexes $(Cp^*\text{–}d_{15})_2Hf(CH_2C_6H_5)_2$ (**2b**), $Cp^*_2Hf(CD_2C_6D_5)_2$ (**2c**), $Cp^*_2Hf(CD_2C_6H_5)_2$ (**2d**), and $Cp^*_2Hf(CH_2C_6D_5)_2$ (**2e**) were prepared as shown in equation 3.

$$\{\eta^5\text{–}C_5(CX_3)_5\}_2HfCl_2 \; + \; 2\,KCY_2C_6Z_5 \xrightarrow{-\,2\,KCl} \{\eta^5\text{–}C_5(CX_3)_5\}_2Hf(CY_2C_6Z_5)_2 \qquad (3)$$

2 ; X = Y = Z = H
2b; X = D, Y = Z = H
2c; X = H, Y = Z = D
2d; X = Z = H, Y = D
2e; X = Y = H, Z = D

Thermal decomposition of **2e** at 140°C occurs at roughly the same rate as **2** ($k_H/k_D = 1.07$) and produces *ca.* 95% $C_6D_5CH_3$[16] (Table 1). A moderate deuterium kinetic isotope effect is observed ($k_H/k_D = 3.1$) when the benzyl methylene groups are deuterated (**2d**), and the toluene produced upon decomposition is approximately 85% $C_6H_5CD_3$. Perdeuteration of the pentamethylcyclopentadienyl rings (**2b**) results in a small deuterium kinetic isotope effect ($k_H/k_D = 1.1$) and *ca.* 95% $C_6H_5CH_3$.

The magnitudes of the kinetic deuterium isotope effects and the labeling of the toluene obtained for the thermal decomposition of compounds **2b–e** indicate a principal pathway involving a rate–limiting α–H abstraction process (Scheme 1), rather than direct transfer of an *ortho*–benzylic hydrogen to the adjacent benzyl group.



Scheme 1. Major pathway for the thermal decomposition of $Cp^*_2Hf(CH_2C_6H_5)_2$ (**2**).

Table 1. Rates of Decomposition of **2**, and **2b–e** (equation 2) and the Isotopically Labeled Toluenes Produced (140°C, C_6D_6).

Compound	$k(10^{-6}s^{-1})$	k_H/k_D	Toluene[a]
2	5.81(19)	----	$C_6H_5CH_3$
2b	5.29(27)	1.1(1)	95% $C_6H_5CH_3$
2c	2.29(6)	2.5(2)	80% $C_6D_5CD_3$ 20% $C_6D_5CD_2H$
2d	1.88(6)	3.1(2)	85% $C_6H_5CD_3$ 15% $C_6H_5CD_2H$
2e	5.40(18)	1.1(1)	95% $C_6D_5CH_3$

[a] Approximate ratio of labeled toluenes were determined by ^1H NMR analysis of the product toluene methyl resonance.

Particularly indicative of this pathway are the moderate kinetic deuterium isotope effect observed for the decomposition of $Cp^*_2Hf(CY_2C_6H_5)_2$ (Y = H, **2**; Y = D, **2d**), and the formation of α–d_3 toluene for **2d**. Thus, the hafnium benzylidene complex **8** is implicated as an intermediate. Moreover, the observation of deuterium (^2H NMR) in the Cp* ligands of metallacycle product **5** upon thermolysis of $Cp^*_2Hf(CD_2C_6D_5)_2$ (**2c**) suggests the intermediacy of **9**, which could arise from **8** by pentamethylcyclopentadienyl ring–hydrogen abstraction. Transfer of an *ortho*–benzylic hydrogen of **9** to the (η^5,η^1–$C_5Me_4CH_2$) ligand finally generates the observed product

$Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$ (5).

The activation parameters for the thermal decomposition of **2**, over the temperature range 125–148°C (Table 2), $\Delta H^\ddagger = 34(1)\ kcal\ mol^{-1}$; $\Delta S^\ddagger = +1(3)$ e.u., are similar to those measured for an analogous (rate-limiting) α–hydrogen abstraction process in the thermal decomposition of $Cp^*_2Ti(CH_3)_2$ to $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)TiCH_3$ and methane ($\Delta H^\ddagger = 27\ kcal{\cdot}mol^{-1}$; $\Delta S^\ddagger = -2.9$ e.u.).[17] The conversion of **8** to **9** is similar to that reported by

Table 2. Rate Data and Activation Parameters for the Thermal Decomposition of $Cp^*_2Hf(CH_2C_6H_5)_2$ (**2**) (benzene–d_6)

Temperature (°C)	$k(10^{-6}s^{-1})$
125	1.11(5)
132.5	2.86(10)
140	5.81(19)
148	14.5(9)

$\Delta H^\ddagger$ = 34(±1) kcal/mol

$\Delta S^\ddagger$ = 1(±3) e.u.

Rothwell *et al.* for the intramolecular addition of an aliphatic C–H bond across a tantalum–carbon double bond.[18]

The appearance of *ca.* 20% $C_6D_5CD_2H$ from the thermolysis of $Cp^*_2Hf(CD_2C_6D_5)_2$ (**2c**) in benzene–d_6 indicates that direct abstraction of a pentamethylcyclopentadienyl ring–hydrogen by a departing hafnium benzyl ligand, generating intermediate **9** without the intermediacy of **8**, is a competitive pathway for the decomposition of $Cp^*_2Hf(CH_2C_6H_5)_2$. This minor pathway is likely to be most prominent when the α–hydrogen abstraction is slowed by deuteration of the benzyl methylene groups as in **2c** and **2d**. Also consistent with direct pentamethylcyclopentadienyl ring–hydrogen abstraction being a relatively minor pathway is the small deuterium kinetic isotope effect observed upon the thermolysis of $(Cp^*–d_{15})_2Hf(CH_2C_6H_5)_2$ (**2b**).

The proposed intermediate **9** and its *meta*–substituted analogs **13–15** can be prepared independently in high yields by the route shown in equations 4–6.

$$Cp^{*}_{2}HfI_{2} + LiCH_{2}CMe_{3} \longrightarrow Cp^{*}_{2}Hf(CH_{2}CMe_{3})I + Li^{+}I^{-} \qquad (4)$$

$$Cp^{*}_{2}Hf(CH_{2}CMe_{3})I \xrightarrow{140^{\circ}C} Cp^{*}(\eta^{5},\eta^{1}-C_{5}Me_{4}CH_{2})HfI + C(CH_{3})_{4} \qquad (5)$$

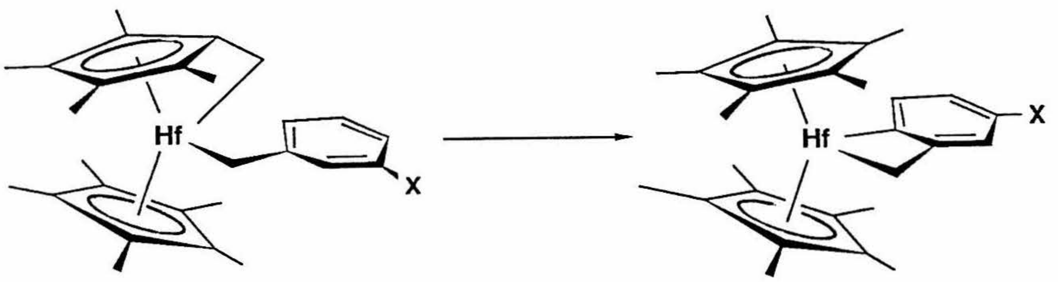
$$Cp^{*}(\eta^{5},\eta^{1}-C_{5}Me_{4}CH_{2})HfI \xrightarrow[-\,M^{+}I^{-}]{+\,MCH_{2}C_{6}H_{4}-m-X} Cp^{*}(\eta^{5},\eta^{1}-C_{5}Me_{4}CH_{2})Hf(CH_{2}C_{6}H_{4}-m-X) \qquad (6)$$

9; X = H
13; X = CH_3
14; X = CF_3
15; X = NMe_2

M = K or MgCl

A moderate deuterium kinetic isotope effect (k_H/k_D at 140°C = 3.75) is observed upon thermolysis of $(Cp^{*}-d_{15})_{2}Hf(CH_{2}CMe_{3})I$, suggesting that formation of $Cp^{*}(\eta^{5},\eta^{1}-C_{5}Me_{4}CH_{2})HfI$ proceeds by the rate–limiting coupling of the neopentyl ligand and a pentamethylcyclopentadienyl ring–hydrogen.

In benzene solution compounds **9** and **13-15** readily rearrange to hafnabenzocyclobutenes **5–7** and **16**, but unlike the thermally robust dibenzyl complexes **2–4**, this conversion occurs slowly over several days at room temperature (equation 7).



(7)

9, 13-15

5, X = H
6, X = CH_3
7, X = NMe_2
16, X = CF_3

The lack of reactivity of the pentamethylcyclopentadienyl–metallated iodide derivative $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ towards benzene (and benzene–d_6) solvent, even on prolonged heating at 140°C, is striking evidence of the tremendous kinetic advantage that *intra*molecular C–H bond activation has over *inter*molecular C–H activation for these sterically encumbered permethylhafnocene derivatives.[19]

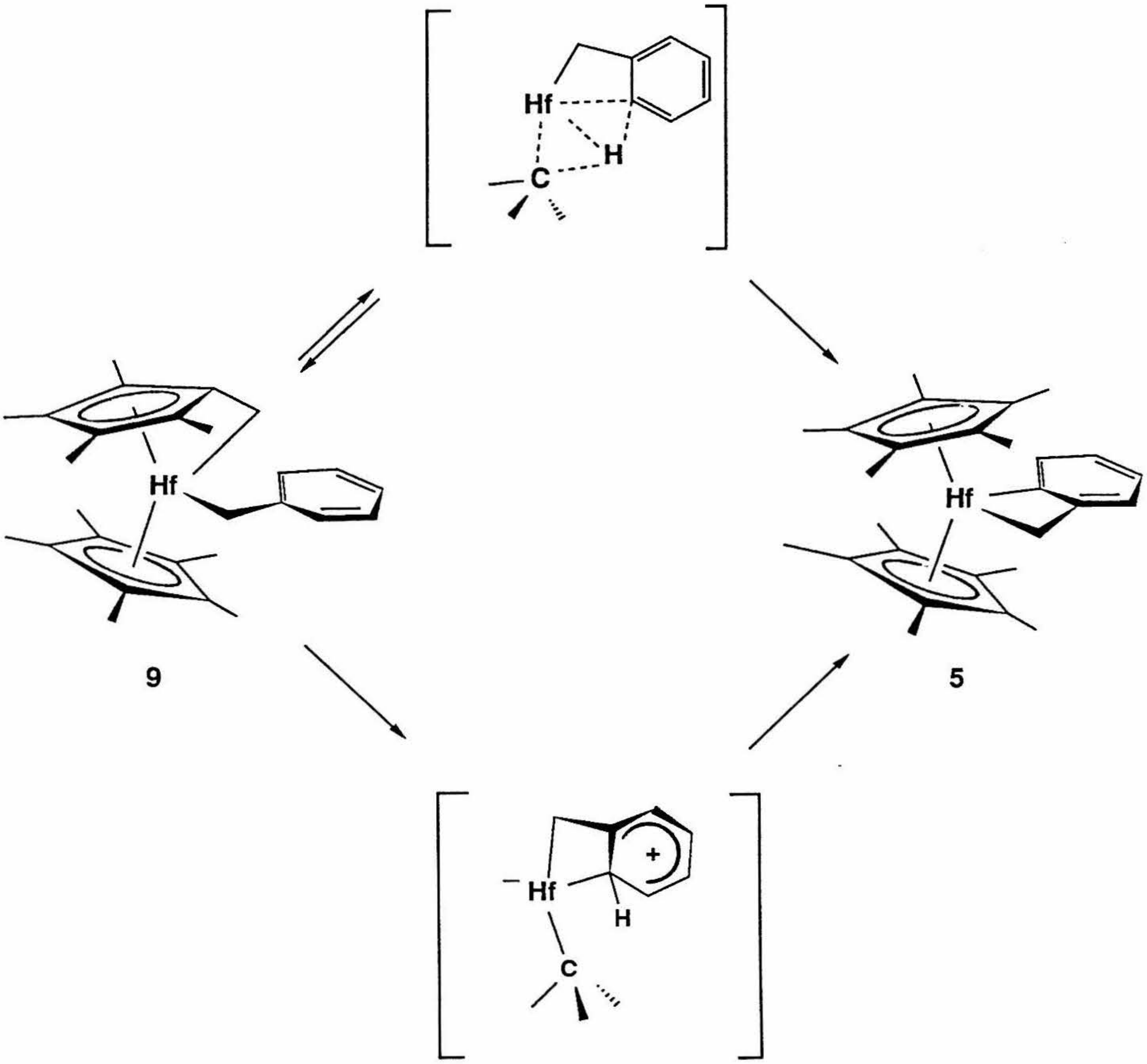
$Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCD_2C_6D_5$ (**9**–d_7), obtained by treating $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ with benzylpotassium–d_7, decomposes much more slowly than $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$ (k_H/k_D = 9.6 at 59°C), consistent with benzylic C–H or C–D bond cleavage in the rate–determining step. Deuterium is observed in the pentamethylcyclopentadienyl ligand (^2H NMR) of the hafnabenzocyclobutene **5**–d_7 derived from **9**–d_7. Steric factors should favor activation of the benzylic hydrogen which is *para* rather than *ortho* to the substituent X in **13–15**, and high field ^1H NMR spectra (400 MHz) of **6**, **7** and **16** indicate X is, indeed, *para* to hafnium (Table 3). Moreover, the rate of conversion of **9** (X = H) to metallacycle **5** is roughly twice that measured for the conversion of **13-15** to metallacycles **6**, **7** and **16**, since the concentration of reactive (sterically unencumbered) C–H bonds for **9** is twice that of the compounds where $X \neq H$.

Kinetic data and activation parameters for the rearrangement of the cyclopentadienyl-metallated benzyl derivatives **9** and **13-15** to the corresponding metallacycles **5–7** and **16** are given in Table 4. As can be seen, the rates of decomposition are nearly independent of the nature of X, and a plot of log k (at 32°C) *versus* the Hammett constants σ_{para}[20] gives a reasonably linear fit with $\rho = -0.2$.[21] Whereas the sign of ρ is in agreement with an electrophilic aromatic substitution mechanism, its small value argues against this pathway for the decomposition of **9** and **13-15**, in spite of the electrophilic nature of the hafnium center. Values of ρ for electrophilic aromatic substitution by cationic organic and inorganic electrophiles typically range from –1.5 to –12.[17,22] Unfavorable steric interactions between the benzyl ligand and the two pentamethylcyclopentadienyl ligands likely prevent the arene from coordinating to the hafnium center with its π system aligned with the vacant orbital on the permethylhafnocene moiety, as would be required for an electrophilic aromatic substitution mechanism. Similar, unfavorable steric interactions were invoked to reconcile the *non*–involvement of the π system in "sigma bond metathesis" reactions between $(\eta^5\text{–}C_5Me_5)_2Sc\text{–}CH_3$ and substituted arenes C_6H_5X (X = CF_3, H, CH_3, OCH_3, NMe_2) to yield $(\eta^5\text{–}C_5Me_5)_2Sc\text{–}C_6H_4X$ and methane.[1b] Moreover, models suggest considerable ring strain accompanies the transition state for the lower pathway of Scheme 2.

Table 4. Rate Constants and Activation Parameters for the Thermal Conversion of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)Hf(CH_2C_6H_4\text{–m–}X)$ to **5-7** and **16** (benzene–d_6).

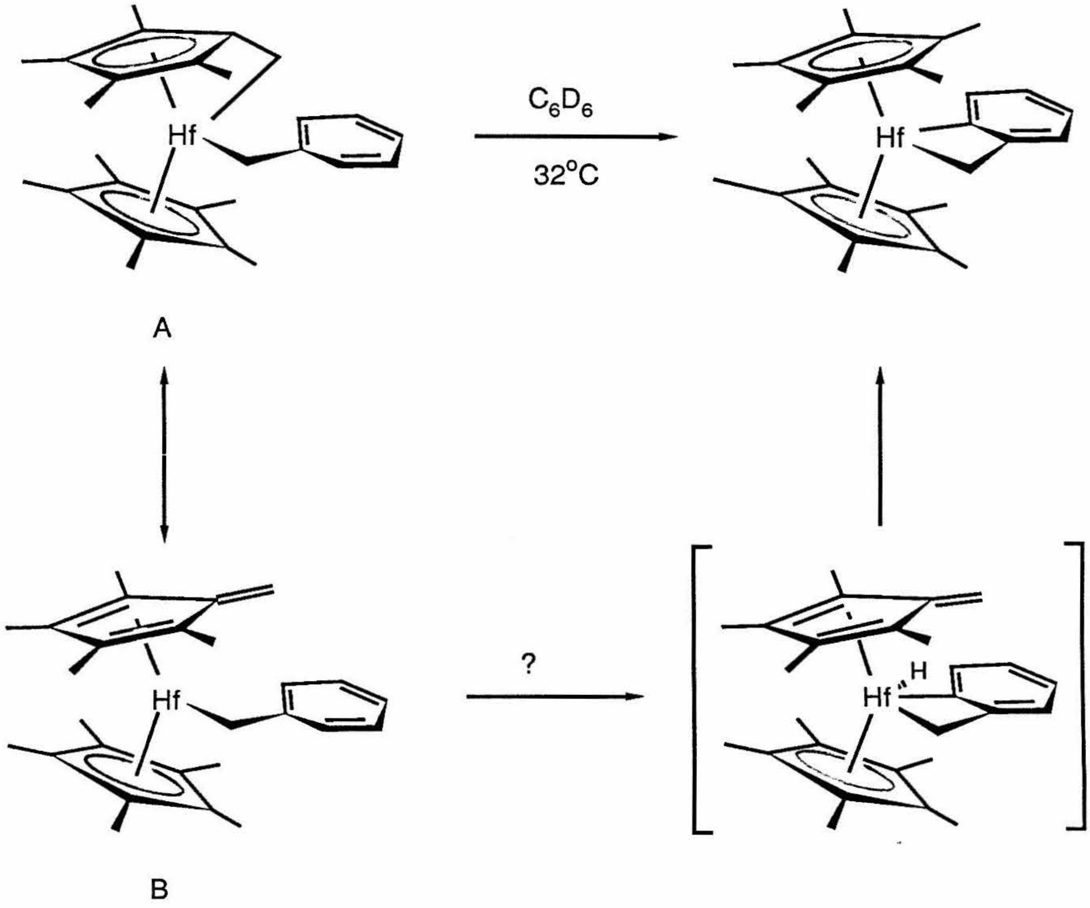
X	T(°C)	$k(10^{-6}s^{-1})$	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (e.u.)
H			20.2(3)	−17.1(7)
	32	3.55(10)		
	48	19.6(6)		
	59	60.4(13)		
CH_3			21.6(3)	−14.1(6)
	32	1.69(12)		
	48	11.2(4)		
	59	34.9(9)		
CF_3			20.3(6)	−17.9(17)
	32	2.07(8)		
	48	12.2(6)		
	59	35.8(13)		
$N(CH_3)_2$			22.0(4)	−12.4(11)
	32	2.16(9)		
	48	15.5(6)		
	59	46.3(13)		

Thus, the mechanism for conversion of $\mathrm{Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)Hf\text{–}CH_2C_6H_5}$ to $\mathrm{Cp^*{}_2\overline{HfCH_2\text{–}\mathit{o}\text{–}C}_6H_4}$ appears to involve attack of hafnium at an *ortho* benzylic C–H bond with the phenyl ring roughly parallel to the metallated cyclopentadienyl ligands (upper pathway of Scheme 2).



SCHEME 2. Two potential pathways for the conversion of $\mathrm{Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5}$ (9) to $\mathrm{Cp^*{}_2\overline{HfCH_2\text{–}\mathit{o}\text{–}C}_6H_4}$ (5).

The very small substituent effects for aryl C–H bond activation observed for both permethylscandocene and permethylhafnocene alkyls would appear to indicate similar mechanisms. Sigma bond metathesis involving d^0 $(\eta^5\text{–}C_5Me_5)_2Sc\text{–}R$ derivatives almost certainly proceeds *via* a four–centered, non–redox mechanism, and such reactions of permethylhafnocene alkyls may well proceed in an analogous manner. On the other hand, an oxidative addition/reductive elimination sequence (lower pathway, Scheme 3) must be considered for the cyclopentadienyl–metallated hafnium derivatives **9** and **13-15**, since two limiting resonance forms, $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)Hf^{IV}(CH_2C_6H_4\text{–}m\text{–}X)$ (**A**) and $Cp^*(\eta^6\text{–}C_5Me_4CH_2)Hf^{II}(CH_2C_6H_4\text{–}m\text{–}X)$ (**B**), describe them.



Scheme 3

Thus, a distinction between mechanisms (upper pathway of Scheme 2 or lower pathway of Scheme 3) rests on which of the two limiting resonance forms (**A** or **B**) best describes the ground states of **9** and **13-15.**

NMR data suggest the structure of **9** is intermediate between resonance forms **A** and **B.** The diastereotopic hydrogens of the bridging methylene are coupled to each other with $^2J_{HH}$ = 8.5 Hz, intermediate between typical values for geminal sp^2 and sp^3 hydrogens of 0–3 and 12–15 Hz, respectively. The gated(^{1}H NOE–enhanced) carbon spectrum for **9** exhibits a signal for the methylene carbon at δ 71.2 with $^1J_{CH}$ = 142 Hz, again intermediate between $^1J_{CH}$ values for sp^2 and sp^3 of 125 and 160 Hz, respectively.

In view of the ambiguities in these NMR data, an X–ray crystal structure determination was undertaken in hopes of distinguishing between **A** and **B.** The molecular structure of **9** is shown in Figure 1, and a skeletal view is shown in Figure 2. Unlike the unmetallated (η^5–C_5Me_5) ring in **9**, which has ring C–C distances from 1.414(10) to 1.424(11) Å, the metallated–(η^5–C_5Me_5) C–C distances vary from 1.396(11) to 1.460(11) Å. The variations are *not* indicative of an η^6–fulvene ligand, however. For example, the three carbon-carbon single bonds in the η^6–fulvene formalism average 1.421(11) Å, whereas the two internal carbon–carbon double bonds are insignificantly longer (averaging 1.423(11) Å). The C25M–Hf distance (2.320(9) Å) is only 0.06 Å longer than the C25–Hf distance of 2.258(8) Å, and C25M is bent (an impressive) 37° out of the ring–carbon plane towards Hf. The C25–C25M distance of 1.453(12) Å is somewhat shorter (0.046 Å) than the average ring–carbon to methyl–carbon distance of 1.499(11) Å.

Only recently have compounds containing a coordinated fulvene ligand been structurally characterized for comparison to Cp*(η^5,η^1–$C_5Me_4CH_2$)$HfCH_2C_6H_5$. Marks et al. have described the structure of the closely related zirconium derivative Cp*(η^5,η^1–$C_5Me_4CH_2$)ZrC_6H_5 and concluded that the η^6 ligand has little fulvene

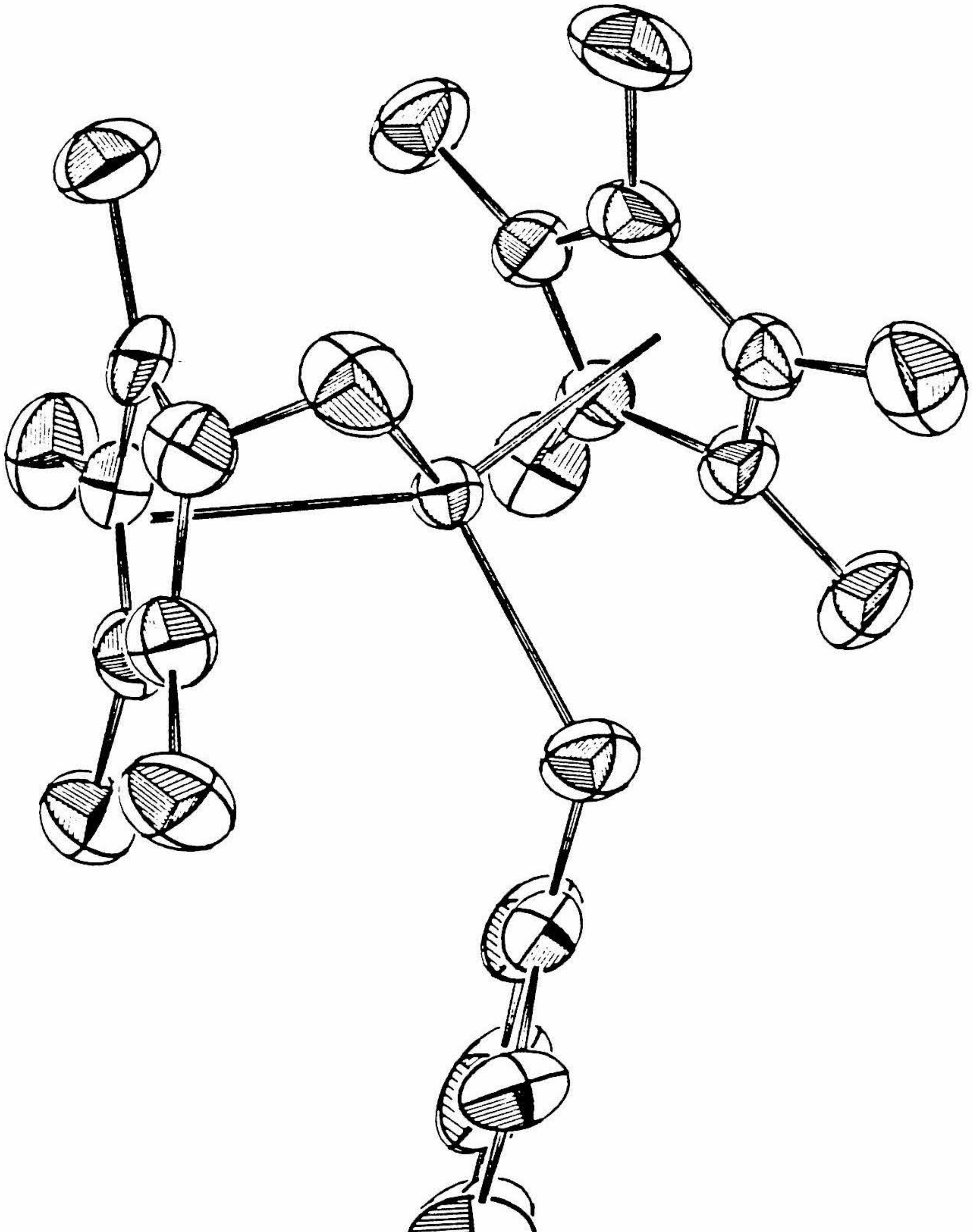


Figure 1. The molecular structure of Cp*(η^5,η^1–$C_5Me_4CH_2$)$HfCH_2C_6H_5$ (**9**). The themal ellipsoids are shown at the 50% probability level.

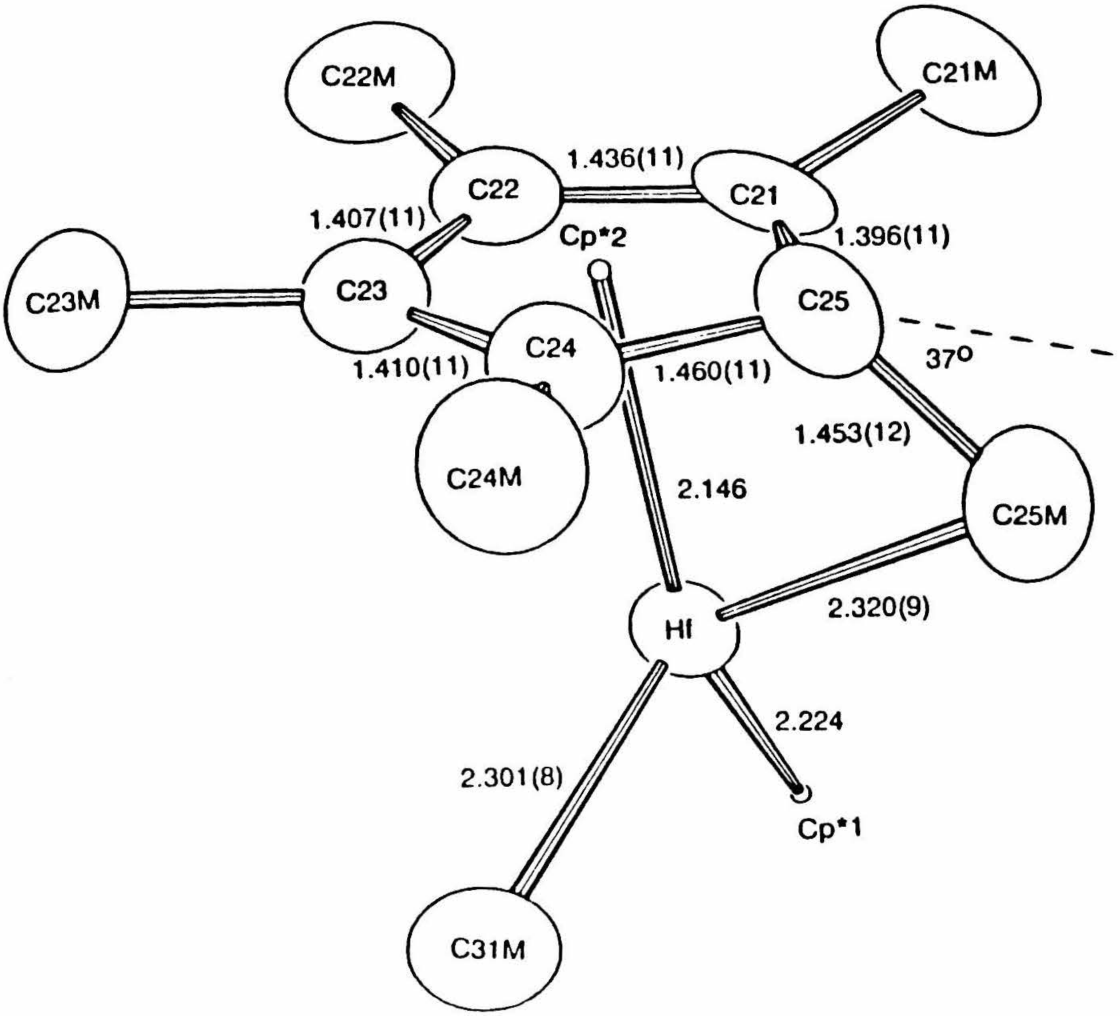


Figure 2. A skeletal view of Cp*(η^5,η^1–$C_5Me_4CH_2$)$HfCH_2C_6H_5$ (**9**).

character.[23] Green and co–workers reported a series of fulvene complexes of the type $M(\eta^5,\eta^1{-}C_5H_4CR_2)(\eta^6{-}C_6H_5R')$ (M = Mo or W; R = CH_3 or C_6H_5; R' = H or CH_3).[24] Based on ring–carbon to methylene–carbon distances of 1.42(2) to 1.45(3) Å and values of θ[25] ranging from 36 to 39°, these authors concluded the metal–fulvene moiety is better described as $M^{II}(\eta^5,\eta^1{-}C_5H_4CR_2)$ than as $M^0(\eta^6{-}C_5H_4CR_2)$. The similar structural features found for the tetramethylfulvene moiety for $Cp^*(\eta^5,\eta^1{-}C_5Me_4CH_2)HfCH_2C_6H_5$ would, by extension of Green's reasoning, argue for $Cp^*(\eta^5,\eta^1{-}C_5Me_4CH_2)Hf^{IV}(CH_2C_6H_4{-}m{-}X)$ (resonance form **A**) structures for **9** and **13-15**.[26]

Conclusions

Labeling experiments demonstrate that the thermal decomposition of $Cp^*{}_2Hf(CH_2C_6H_5)_2$ (**2**) occurs primarily by an α–H abstraction process to generate a transient hafnium benzylidene species, which rearranges to the metallated–cyclopentadienyl benzyl complex $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$ (**9**), and finally to the observed hafnabenzocyclobutene $Cp^*{}_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$ (**5**). A convenient starting material for the synthesis of a series of metallated–cyclopentadienyl derivatives of permethylhafnocene is $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$, obtained in high yield by the pyrolysis of $Cp^*{}_2Hf(CH_2CMe_3)I$. The small rate differences among the series of complexes $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)Hf(CH_2C_6H_4\text{–}m\text{–}X)$ ($X = CF_3$, H, CH_3, NMe_2) and the relatively large negative values for the activation entropies indicate that the thermal rearrangement of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$ to $Cp^*{}_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$ occurs by a highly ordered, four–centered transition state, similar to that observed for intermolecular, sigma bond metathesis reactions involving arenes and permethylscandocene alkyls.[1b] Specifically, the cleavage of the aryl C–H bond occurs by direct attack of the electrophilic hafnium center at the carbon–hydrogen σ bond, without interaction of the π orbitals of the arene (*i.e.* according to the upper pathway of Scheme 2).

Table 3. ^{1}H and ^{13}C NMR data^{a}

Compound	Assignment	δ(ppm)^{b}	coupling^{c}
$Cp^{*}_{2}Hf(CH_2C_6H_5)_2$ **(2)**			
	$\eta^5\text{-}C_5(\mathrm{C}H_3)_5$	1.77 s	
	$\mathrm{C}H_2\mathrm{C_6H_5}$	1.41 br	
	$\mathrm{CH_2C_6}H_5$	6.83–7.33 m	
$Cp^{*}_{2}Hf(CH_2C_6H_4\text{–}m\text{–}CH_3)_2$ **(3)**			
	$\eta^5\text{-}C_5(\mathrm{C}H_3)_5$	1.78 s	
	$\mathrm{C}H_2\mathrm{C_6H_4CH_3}$	1.44 br	
	$\mathrm{CH_2C_6H_4C}H_3$	2.27 s	
	$\mathrm{CH_2C_6}H_4\mathrm{CH_3}$	6.73–7.27 m	
$Cp^{*}_{2}Hf(CH_2C_6H_4\text{–}m\text{–}NMe_2)_2$ **(4)**			
	$\eta^5\text{-}C_5(\mathrm{C}H_3)_5$	1.83 s	
	$\mathrm{C}H_2\mathrm{C_6H_4NMe_2}$	1.50 br	
	$\mathrm{CH_2C_6}H_4\mathrm{NMe_2}$	6.37–7.30 m	
	$\mathrm{CH_2C_6H_4N(C}H_3)_2$	2.71 s	
$Cp^{*}_{2}\overline{HfCH_2\text{–}o\text{–}C}_6H_4$ **(5)**			
	$\eta^5\text{-}C_5(\mathrm{C}H_3)_5$	1.68 s	
	$\mathrm{C}H_2\mathrm{C_6H_4}$	2.30 br	
	$\mathrm{CH_2C_6}H_4$	7.03–7.80 m	
$Cp^{*}_{2}\overline{HfCH_2\text{–}o\text{–}C}_6H_3\text{–}m\text{–}Me$ **(6)**			
	$\eta^5\text{-}C_5(\mathrm{C}H_3)_5$	1.62 s	
	$\mathrm{C}H_2\mathrm{C_6H_3CH_3}$	2.13 br	
	$\mathrm{CH_2C_6}H_3\mathrm{CH_3}$	7.52 s	
		7.44 d	$^{3}J_{HH}$=7.0
		7.10 d	$^{3}J_{HH}$=7.0
	$\mathrm{CH_2C_6H_3C}H_3$	2.16 s	
$Cp^{*}_{2}\overline{HfCH_2\text{–}o\text{–}C}_6H_3\text{–}m\text{–}NMe_2$ **(7)**			
	$\eta^5\text{-}C_5(\mathrm{C}H_3)_5$	1.75 s	
	$\mathrm{C}H_2\mathrm{C_6H_3NMe_2}$	2.37 br	
	$\mathrm{CH_2C_6}H_3\mathrm{NMe_2}$	7.48 d	$^{3}J_{HH}$=7.6
		7.18 d	$^{4}J_{HH}$=2.2
		6.81 dd	$^{3}J_{HH}$=7.6 $^{4}J_{HH}$=2.2
	$\mathrm{CH_2C_6H_3N(C}H_3)_2$	2.72 s	

$\mathrm{Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)Hf(CH_2C_6H_5)}$ **(9)**

$\eta^5\mathrm{–C_5(C}\mathit{H}_3\mathrm{)_5}$	1.88 s	
$\mathrm{C_5(CH_3)_4C}\mathit{H}_2$	1.54 d	$^2J_{HH}$=7.6
	1.96 d	$^2J_{HH}$=7.6
$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2}$	1.43 s	
	1.52 s	
	1.67 s	
	1.95 s	
$\mathrm{C}\mathit{H}_2\mathrm{C_6H_5}$	–0.33 d	$^2J_{HH}$=14.4
	2.13 d	$^2J_{HH}$=14.4
$\mathrm{CH_2C_6}\mathit{H}_5$	6.85–7.15 m	
$\mathit{C}\mathrm{H_2C_6H_5}$	57.25 t	$^1J_{CH}$=113
$\eta^5\mathrm{–C_5(}\mathit{C}\mathrm{H_3)_5}$	12.19 q	$^1J_{CH}$=125
$\eta^5\mathrm{–}\mathit{C}_5\mathrm{(CH_3)_5}$	117.5 s	
$\mathrm{C_5(CH_3)_4}\mathit{C}\mathrm{H_2}$	71.24 t	$^1J_{CH}$=142

$\mathrm{Cp^*_2Hf(CH_2CMe_3)I}$ **(11)**

$\eta^5\mathrm{–C_5(C}\mathit{H}_3\mathrm{)_5}$	2.00 s	
$\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_3}$	0.02 s	
$\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)_3}$	1.27 s	

$\mathrm{Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)HfI}$ **(12)**

$\eta^5\mathrm{–C_5(CH_3)_5}$	1.96 s	
$\mathrm{C_5(CH_3)_4C}\mathit{H}_2$	1.42 d	$^2J_{HH}$=7.8
	1.99 d	$^2J_{HH}$=7.8
$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2}$	1.53 s	
	1.69 s	
	1.98 s	
	2.40 s	
$\eta^5\mathrm{–C_5(}\mathit{C}\mathrm{H_3)_5}$	13.22 q	$^1J_{CH}$=126
$\eta^5\mathrm{–}\mathit{C}_5\mathrm{(CH_3)_5}$	118.91 s	
$\mathrm{C_5(CH_3)_4}\mathit{C}\mathrm{H_2}$	74.9 t	$^1J_{CH}$=144

$\mathrm{Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)Hf(CH_2C_6H_4–m–CH_3)}$ **(13)**

$\eta^5\mathrm{–C_5(C}\mathit{H}_3\mathrm{)_5}$	1.90 s	
$\mathrm{C_5(CH_3)_4C}\mathit{H}_2$	1.55 d	$^2J_{HH}$=7.5
	1.88 d	$^2J_{HH}$=7.5
$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2}$	1.44 s	
	1.55 s	
	1.69 s	
	1.96 s	
$\mathrm{C}\mathit{H}_2\mathrm{C_6H_4CH_3}$	–0.30 d	$^2J_{HH}$=13.8
	1.91 d	$^2J_{HH}$=13.8
$\mathrm{CH_2C_6H_4C}\mathit{H}_3$	2.22 s	
$\mathrm{CH_2C_6}\mathit{H}_4\mathrm{CH_3}$	6.43–7.07 m	
$\mathit{C}\mathrm{H_2C_6H_4CH_3}$	56.93 t	$^1J_{CH}$=113
$\eta^5\mathrm{–C_5(}\mathit{C}\mathrm{H_3)_5}$	12.22 q	$^1J_{CH}$=125

$\eta^5\mathrm{-}\mathit{C}_5\mathrm{(CH_3)_5}$	117.49 s	
$\mathrm{C_5(CH_3)_4}\mathit{C}\mathrm{H_2}$	71.09 t	$^1J_{CH}$=142
Cp*(η^5,η^1–$\mathrm{C_5Me_4CH_2}$)Hf($\mathrm{CH_2C_6H_4}$–m–$\mathrm{CF_3}$) (**14**)		
$\eta^5\mathrm{-C_5(C}\mathit{H}_3\mathrm{)_5}$	1.84 s	
$\mathrm{C_5(CH_3)_4C}\mathit{H}_2$	1.50 d	$^2J_{HH}$=7.6
	1.89 d	$^2J_{HH}$=7.6
$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2}$	1.28 s	
	1.47 s	
	1.61 s	
	1.83 s	
$\mathrm{C}\mathit{H}_2\mathrm{C_6H_4CF_3}$	–0.45 d	$^2J_{HH}$=14.0
	1.87 d	$^2J_{HH}$=14.0
$\mathrm{CH_2C_6}\mathit{H}_4\mathrm{CF_3}$	6.80–7.12 m	
$\eta^5\mathrm{-C_5(}\mathit{C}\mathrm{H_3)_5}$	12.10 q	$^1J_{CH}$=125
$\eta^5\mathrm{-}\mathit{C}_5\mathrm{(CH_3)_5}$	117.78 s	
$\mathit{C}\mathrm{H_2C_6H_4CF_3}$	55.93 t	$^1J_{CH}$=113
$\mathrm{C_5(CH_3)_4}\mathit{C}\mathrm{H_2}$	71.51 t	$^1J_{CH}$=142
Cp*(η^5,η^1–$\mathrm{C_5Me_4CH_2}$)Hf($\mathrm{CH_2C_6H_4}$–m–$\mathrm{NMe_2}$) (**15**)		
$\eta^5\mathrm{-C_5(C}\mathit{H}_3\mathrm{)_5}$	1.91 s	
$\mathrm{C_5(CH_3)_4C}\mathit{H}_2$	1.58 d	$^2J_{HH}$=7.5
	2.03 d	$^2J_{HH}$=7.5
$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2}$	1.53 s	
	1.55 s	
	1.68 s	
	2.04 s	
$\mathrm{CH_2C_6H_4N(C}\mathit{H}_3\mathrm{)_2}$	2.67 s	
$\mathrm{C}\mathit{H}_2\mathrm{C_6H_4N(CH_3)_2}$	–0.30 d	$^2J_{HH}$=14.0
	2.13 d	$^2J_{HH}$=14.0
$\mathrm{CH_2C_6}\mathit{H}_4\mathrm{N(CH_3)_2}$	6.15–7.10 m	
$\eta^5\mathrm{-C_5(}\mathit{C}\mathrm{H_3)_5}$	12.24 q	$^1J_{CH}$=125
$\eta^5\mathrm{-}\mathit{C}_5\mathrm{(CH_3)_5}$	117.45 s	
$\mathit{C}\mathrm{H_2C_6H_4N(CH_3)_2}$	57.82 t	$^1J_{CH}$=113
$\mathrm{C_5(CH_3)_4}\mathit{C}\mathrm{H_2}$	71.12 t	$^1J_{CH}$=142
$\mathrm{Cp^*{}_2\overline{HfCH_2{-}o{-}C}_6H_3{-}m{-}CF_3}$ (**16**)		
$\eta^5\mathrm{-C_5(C}\mathit{H}_3\mathrm{)_5}$	1.54 s	
$\mathrm{C}\mathit{H}_2\mathrm{C_6H_3CF_3}$	2.03 br	
$\mathrm{CH_2C_6}\mathit{H}_3\mathrm{CF_3}$	7.87 s	
	7.46 d	$^3J_{HH}$=7.3
	7.34 d	$^3J_{HH}$=7.3

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[a] NMR spectra were recorded in benzene–d_6 at ambient temperature. [b] Chemical shifts are reported in parts per million (δ) from tetramethylsilane. [c] Coupling constants are reported in hertz.

Table 5. Crystal Data for Cp*(η^5,η^1–$C_5Me_4CH_2$)$HfCH_2C_6H_5$ (**9**).

formula: $HfC_{27}H_{36}$		f.wt. 539.08
Space group $P\bar{1}$		T = 21°C
z = 2		V = 1161(1) Å^3
a = 9.084(2) Å	α = 95.81(1)°	
b = 10.492(2) Å	β = 96.60(1)°	ρ_c = 1.543(1) g/cc
c = 12.328(1) Å	γ = 91.15(2)°	
λ MoKα = 0.71073 Å		μ(MoKα) = 47.5 cm^{-1}
F(000) = 540 e		μr_{max} = 1.70
Crystal size 0.55 x 0.31 x 0.34 mm		

Table 6. Final Parameters[a]

	x	y	z	U_{eq}[b]
Hf	2076.9(3)	1815.0(3)	2536.0(2)	30.6(1)
C11	3978(8)	1619(8)	4177(6)	43(2)
C12	3182(8)	421(8)	3949(6)	46(2)
C13	3510(8)	−152(7)	2918(6)	43(2)
C14	4532(8)	667(7)	2521(6)	41(2)
C15	4775(7)	1776(7)	3279(6)	39(2)
C11M	4250(10)	2401(10)	5265(7)	67(3)
C12M	2344(11)	−213(10)	4729(9)	73(3)
C13M	2971(11)	−1439(9)	2369(8)	67(3)
C14M	5393(10)	315(10)	1577(7)	61(2)
C15M	5889(9)	2855(9)	3222(8)	62(2)
C21	771(9)	3245(8)	3721(7)	48(2)
C22	1629(9)	4155(7)	3240(6)	45(2)
C23	1106(8)	4050(7)	2114(7)	45(2)
C24	−15(8)	3080(8)	1879(7)	44(2)
C25	−166(8)	2520(8)	2899(7)	47(2)
C21M	761(11)	3157(11)	4942(7)	68(3)
C22M	2660(11)	5199(9)	3805(8)	66(3)
C23M	1531(11)	4949(8)	1320(8)	61(2)
C24M	−1005(9)	2755(9)	831(8)	61(2)
C25M	−256(9)	1133(9)	2876(8)	58(2)
C31	2395(9)	2036(8)	−149(6)	48(2)
C32	1491(12)	2100(10)	−1124(7)	67(3)
C33	1852(20)	2879(15)	−1896(9)	107(5)
C34	3154(24)	3572(14)	−1746(13	119(5)
C35	43703(12)	2770(9)	9(8)	67(2)
C31M	1999(9)	1197(8)	685(6)	48(2)

[a] x, y, z X10^4; U_{eq} X10^3

[b] $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij}(a_i^* a_j^*) a_i^* \cdot a_j^*$; $\sigma U_{eq} = 6^{-1/2} <\sigma U_{ii}/U_{ii}> U_{eq}$

Table 7. Selected Distances and Angles

Atom	Atom	Dist. (Å)	Atom	Atom	Atom	Angle
Hf	C21	2.412(8)	C22	C21	C25	109.7(7)
Hf	C22	2.576(8)	C22	C21	C21M	125.7(7)
Hf	C23	2.603(8)	C25	C21	C21M	124.4(7)
Hf	C24	2.448(8)	C21	C22	C23	106.6(7)
Hf	C25	2.258(8)	C21	C22	C22M	128.4(7)
Hf	C25M	2.320(9)	C23	C22	C22M	124.0(7)
Hf	C31M	2.301(8)	C22	C23	C24	109.5(7)
C21	C22	1.436(11)	C22	C23	C23M	125.0(7)
C21	C25	1.396(11)	C24	C23	C23M	125.1(7)
C21	C21M	1.519(13)	C23	C24	C25	107.3(7)
C22	C23	1.407(11)	C23	C24	C24M	127.7(7)
C22	C22M	1.489(13)	C25	C24	C24M	124.6(7)
C23	C24	1.410(11)	C21	C25	C24	106.5(7)
C23	C23M	1.501(12)	C21	C25	C25M	120.1(7)
C24	C25	1.460(11)	C24	C25	C25M	118.8(7)
C24	C24M	1.492(12)	C31M	Hf	C25M	101.5(3)
C25	C25M	1.453(12)	Cp*1	Hf	Cp*2	141.6
Hf	Cp*1	2.224	Cp*1	Hf	C25M	116.3
Hf	Cp*2	2.146	Cp*1	Hf	C31M	107.0
			Cp*2	Hf	C25M	69.1
			Cp*2	Hf	C31M	108.9
			Cp*2	C25	C25M	142.7
			C25	Cp*2	Hf	79.0
			C25M	Cp*2	Hf	58.7

Cp*1 and Cp*2 are the centroid coordinates of C11 through C15 and C21 through C25 Cp* rings, respectively.

Experimental Section

General Considerations. All manipulations were performed using glovebox or high vacuum techniques. Solvents were purified by distillation from Na metal under an N_2 atmosphere followed by vacuum transfer from "titanocene". NMR solvents were purified by vacuum transfer from activated molecular sieves (4 Å, Linde) and then from "titanocene". ^1H, ^2H, and ^{13}C NMR spectra were obtained by using Varian EM–390 (90 MHz, ^1H) and JEOL GX400Q (400 MHz, ^1H; 100 MHz, ^{13}C; 60.4 MHz, ^2H) spectrometers. Elemental analyses were performed by Larry Henling of the CIT Analytical Laboratory.

Procedures.

$Cp^*{}_2Hf(CH_2C_6H_5)_2$ (2). Permethylhafnocene dichloride **1** (1.40 g, 2.70 mmol) and $KCH_2C_6H_5$ (0.95 g, 7.31 mmol) were stirred overnight in 20 mL of benzene. Following filtration the benzene was replaced with 10 mL of petroleum ether. Cooling to –78°C and filtering yielded 0.90 g (52 %) of yellow **2**. Anal. Calcd. for $HfC_{34}H_{44}$: C, 64.73; H, 6.97. Found: C, 64.93; H, 6.85. The isotopically labeled bis(benzyl) compounds **2b–e** were prepared in an analogous manner from the appropriately labeled starting materials.

Preparation of $(Cp^*\text{–}d_{15})_2HfI_2$. To a large glass bomb was added $Cp^*{}_2HfH_2$ (0.46 g, 1.0 mmol) and *ca.* 10 mL of benzene–d_6. Deuterium gas admitted into the apparatus at –196°C. This solution was heated to 115°C with stirring for 5 days. The bomb was recharged daily with fresh deuterium gas. At the end of 5 days excess CH_3I was condensed into the bomb resulting in the rapid formation of $(Cp^*\text{–}d_{15})_2HfI_2$, which was isolated from petroleum ether (0.39 g, 55%). The total isotopic purity was ≥95% (^1H NMR).

$Cp^*{}_2Hf(CH_2C_6H_4\text{–}m\text{–}CH_3)_2$ (3). The diiodide derivative $Cp^*{}_2HfI_2$ (1.07 g, 1.52 mmol) and $KCH_2C_6H_4\text{–}m\text{–}CH_3$ (0.69 g, 4.79 mmol) were stirred overnight in *ca.* 20 mL benzene. After filtering, the benzene was replaced with *ca.* 10 mL of petroleum ether. Cooling to –78°C and filtering yielded 0.48 g (48%) of pale yellow **3**. Anal. Calcd. for $HfC_{36}H_{48}$: C, 65.59; H, 7.34. Found: C, 66.31; H, 7.54.

$Cp^*_2Hf(CH_2C_6H_4\text{–}m\text{–}NMe_2)_2$ (4). Compound **1** (1.67 g, 3.21 mmol) and 1.4 g (8.09 mmol) of $KCH_2C_6H_4\text{–}m\text{–}NMe_2$ were stirred overnight in *ca.* 20 mL benzene. After filtering, the benzene was replaced with *ca.* 10 mL of petroleum ether. Cooling to –78°C and filtering yielded 1.75 g (71%) of pale yellow **4**. Anal. Calcd. for $HfC_{38}H_{54}N_2$: C, 63.57; H, 7.66; N, 3.90. Found: C, 63.84; H, 7.52; N, 3.92.

$Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$ (5). To a small glass bomb was added 1.17 g (1.85 mmol) of **2** and *ca.* 10 mL of methylcyclohexane. The solution was heated to 140°C for 6 days. Isolation from petroleum ether yielded 0.61 g of pale yellow **5** (61%). Anal. Calcd. for $HfC_{27}H_{36}$: C, 60.62; Hf, 6.77. Found: C, 60.86; H, 6.84.

$Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_3\text{–}m\text{–}NMe_2$ (7). To a small glass bomb was added compound **4** (0.75 g, 1.0 mmol) and 5 mL of toluene. This solution was heated for 2 days at 145°C. Isolation from –78°C petroleum ether afforded 0.18 g of pale yellow **7** (30%). Anal. Calcd. for $HfC_{29}H_{41}N$: C, 59.83; H, 7.10; N, 2.41. Found: C, 59.31; H, 7.37; N, 2.23.

$Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$ (9). $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ (0.82 g, 1.4 mmol) and $KCH_2C_6H_5$ (0.19 g, 1.5 mmol) were stirred for 1 hour in 10 mL of benzene. After filtering, the benzene was replaced with 10 mL of petroleum ether. Cooling to –78°C and filtering yielded 0.42 g (52%) of yellow orange **9**. Anal. Calcd. for $HfC_{27}H_{36}$: C, 60.16; H, 6.73. Found: C, 60.47; H, 6.74.

$Cp^*_2Hf(CH_2CMe_3)I$ (11). Permethylhafnocene diiodide (0.94 g, 1.5 mmol) and $LiCH_2CMe_3$ (0.13 g, 1.6 mmol) were stirred overnight in benzene. Following filtration the benzene was replaced with 10 mL of petroleum ether. Cooling to –78°C and filtering afforded 0.74 g

(85%) of yellow $Cp^*_2Hf(CH_2CMe_3)I$. Anal. Calcd. for $HfC_{25}H_{41}I$: C, 46.44; H, 6.39. Found: C, 46.15; H, 6.16.

$Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)HfI$ (12). To a small glass bomb was added $Cp^*_2Hf(CH_2CMe_3)I$ (4.24 g, 6.54 mmol) and 30 mL of toluene. This solution was heated at 140°C for 2 days. Isolation from petroleum ether at –78°C yielded 2.1 g (56%) of orange $Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)HfI$. Anal. Calcd. for $HfC_{20}H_{29}I$: C, 41.79; H, 5.08. Found: C, 42.27; H, 5.07.

$Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)Hf(CH_2C_6H_4-m-CH_3)$ (13). $Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)HfI$ (0.90 g, 1.6 mmol) and $KCH_2C_6H_4-m-CH_3$ (0.33 g, 2.29 mmol) were stirred for 1 hour in 20 mL of benzene. Following filtration the benzene was replaced with 5 mL of petroleum ether. Cooling to –78°C and filtering yielded 0.50 g (56%) of yellow orange **10**. Anal. Calcd for $HfC_{28}H_{38}$: C, 60.84; H, 6.87. Found: C, 58.80 ; H, 6.65.

$Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)Hf(CH_2C_6H_4-m-CF_3)$ (14). $Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)HfI$ (0.75 g, 1.30 mmol) and 1.1 equivalents of $ClMgCH_2C_6H_4-m-CF_3$ were stirred in 10 mL of diethyl ether for 1 hour. The solvent was replaced with petroleum ether and the solution was filtered. Cooling to –78°C and filtering yielded 0.57 g (72%) of yellow orange **11**. Anal. Calcd. for $HfC_{28}H_{35}F_3$: C, 55.31; H, 5.97. Found: C, 54.49; H, 5.77.

$Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)Hf(CH_2C_6H_4-m-NMe_2)$ (15). $Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)HfI$ (0.81 g, 1.4 mmol) and $KCH_2C_6H_4-m-NMe_2$ (0.25 g, 1.46 mmol) were stirred for 1 hour in 10 mL of benzene. After filtering the solvent was replaced with petroleum ether. Cooling to –78°C and then filtering afforded 0.37 g (45%) of yellow orange **12**. Anal. Calcd. for $HfC_{29}H_{41}N$: C, 59.83; H, 7.10; N, 2.41. Found: C, 60.23; H, 7.17; N, 2.19.

Kinetic Measurements of Thermal Decomposition. With one exception, all reactions were followed by monitoring the decrease in height of the pentamethylcyclopentadienyl resonance of starting complex relative to internal $(\eta^5\text{–}C_5H_5)_2Fe$. The rate of decomposition of **2b** was followed by monitoring the decrease in integrated intensity of the $(Cp^*\text{–}d_{15})_2Hf(CH_2C_6H_5)_2$ signal relative to $(\eta^5\text{–}C_5H_5)_2Fe$. NMR spectra were recorded at timed intervals using a Varian EM–390 (90 MHz) spectrometer. Reaction temperatures were maintained using constant temperature oil baths controlled by thermoregulators and were observed to be constant to within ±1°C. A typical experiment involved 25 mgs of hafnium complex and 6–10 mg of ferrocene dissolved in 0.4 mL of benzene–d_6. The NMR tubes were sealed containing >1 atm of dinitrogen. Total submersion in the oil bath prevented the benzene–d_6 from refluxing at the elevated temperatures used in this study.

Peak heights were demonstrated to be reproducible to within ±7% by repeated measurement. Each spectrum was recorded 3 times and the average peak height was used to calculate the values of k given in Tables 1,2 and 4. Errors in k represent approximately 1 standard deviation. Plots of ln(k/T) vs. 1/T were constructed from the decomposition rates and yielded the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$. Errors in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ represent 1 standard deviation calculated by error propagation of 1 standard deviation changes in the value of $-\Delta H^\ddagger/R$ and ln(A/T)−1, when the measured k values are varied within their error limits.

X–ray Structure Determination. Crystals of $(\eta^5\text{–}C_5Me_5)(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$ (**9**) were obtained by slow evaporation of a saturated diethyl ether solution and sealed in glass capillaries under dinitrogen to prevent decomposition. Oscillation and zero–, first–, and second–layer Weissenberg photographs showed no evidence of twinning, and the crystal was mounted on a CAD4 diffractometer equipped with graphite–monochromated MoKα radiation. A least–squares fit to the setting angles of 25 reflections (20 of which were independent of one another) with $16^\circ < 2\theta < 26^\circ$ indicated a triclinic cell and yielded the cell parameters. As neither nontrivial symmetry nor systematic absences were observed in the photographs, and since an approximate calculation indicated two molecules per cell, $P\bar{1}$ symmetry was assumed. All data ($\pm h$, $\pm k$, $\pm l$) with $2^{\circ}<2\theta<52^{\circ}$ were collected, and the *hk*0 reflections were collected twice. These data were merged to give 4529 independent observations. Three index reflections monitored every 10,000 seconds of X–ray exposure time showed a linear decay of 1.5% in F over the 136 hours required to collect the data. The data were corrected for this decay, as well as for Lorentz and polarization factors, but no correction was made for absorption due to the rounded shape of the crystal, which made an accurate representation of its shape impractical.

Solution and Refinement. A Wilson plot was used to place the data on an approximately absolute scale. Variances, $\sigma^2(I)$, were assigned to the intensities on the basis of counting statistics plus an additional term, $(0.014\ I)^2$, to account for additional errors proportional to the intensity. A Patterson map yielded hafnium coordinates and successive structure factor–Fourier calculations located the remaining atoms. Refinement with all the heavy atoms anisotropic converged with $R = \Sigma||F_0|-|F_c||/\Sigma|F_0| = 0.048$ for all 4455 reflections with $F_0^2 > 0$ and 0.046 for the 4187 reflections with $F_0^2 > 3\sigma\ (F_0^2)$. The goodness of fit, $[\Sigma w(F_0^2-F_c^2)/(n-p)]^{1/2}$, where n = number of data = 4529 and p = number of parameters = 254, is 4.37[27]. Hydrogen atoms were introduced at idealized positions during the refinement and repositioned two or three times, depending on the accuracy of the initial placement. Non–methyl hydrogen positions were calculated in accordance with expected bond geometry; methyl hydrogens were placed on the basis of Fourier maps in the plane where they were expected. At first the maps did not clearly suggest all hydrogen positions, but by the last cycle the idealized positions where the hydrogens were placed agreed fairly closely with the difference maps. All hydrogens were assigned isotropic temperature factors 1.0 Å^2 greater than the equivalent isotropic factors of the parent carbons. In the final least squares cycle no parameter shifted by more than 0.03 of its standard deviation. Crystal data are given in Table 5 and final parameters in Table 6. Calculations were done using the programs of the CRYM crystallographic computing system[28] on a VAX 11/750 computer; the drawing was done using ORTEP[29].

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(25) θ is defined as the angle by which the exocyclic bond of the fulvene ligand deviates from planarity with the five ring carbons of the cyclopentadienyl ligand. This deviation is towards the metal center.

(26) There are no indications of interaction between the hafnium and the aryl ring of the benzyl ligand (*i.e.* an η^3–$CH_2C_6H_5$ interaction) for **9**, in contrast to the structures of other, analogous benzyl complexes (*vida supra*).

(27) The absorption correction was only approximate because of the irregular shape of the crystal. Because of this, there are large excursions near the hafnium atom in the final difference map (+5.05, -3.43 e Å^3). The high value of the goodness of fit probably results from this also. We believe the weights were chosen properly; a larger "fudge" factor for them (such as 0.05, rather than the 0.02 we used) would improve the goodness of fit, but such a high value is not indicated by the data.

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Chapter 2

Synthesis and Reactivity of Singly and Doubly Metallated Cp* Containing Derivatives of Permethylhafnocene: The Molecular Structure of Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf.

Abstract: Thermolysis of the singly metallated complex Cp*(η^5,η^1–$C_5Me_4CH_2$)Hf(CH_2CMe_3) in toluene affords neopentane and the doubly metallated complex Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf. The structure of Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf, as determined by single–crystal X–ray diffraction techniques, confirms that metallation has occurred at adjacent methyl groups of the same pentamethylcyclopentadienyl ring. Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf crystallizes in the space group P2/c (a = 13.775(4) Å, b = 9.516(1) Å, c = 14.183(6) Å; β = 103.965(31)°, z = 4). Least squares refinement led to a value for R of 0.036 ($I > 3\sigma_I$) and a goodness–of–fit of 2.66 for 1984 independent reflections. Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf and Cp*(η^5,η^1–$C_5Me_4CH_2$)HfI cleanly insert one equivalent of ethylene into the hafnium methylene carbon bond to form the propyl bridged species Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)(CH_2CH_2CH_2)$)Hf and Cp*($\eta^5$,$\eta^1$–$C_5Me_3CH_2CH_2CH_2$)HfI, respectively. Cp*($\eta^5$,$\eta^1$,$\eta^1$–$C_5Me_3(CH_2)(CH_2CH_2CH_2)$)Hf reacts with excess ethylene to cleanly afford Cp*(η^5,η^1,η^1–$C_5Me_4CH_2CH_2CHCH_2CH_2$)Hf. Deuterium labeling experiments suggest that this reaction occurs *via* an α–H abstraction to generate the alkylidene intermediate Cp*(η^5,η^1–$C_5Me_4CH_2CH_2CH$=)Hf, which rapidly traps ethylene to form the observed product. The metallated phenyl complex Cp*(η^5,η^1–$C_5Me_3CH_2$)HfC_6H_5 has been shown to be in equilibrium with the benzyne complex Cp*$_2$Hf(η^2–C_6H_4). Heating benzene–d_6 solutions of Cp*(η^5,η^1–$C_5Me_3CH_2$)HfC_6H_5 in the presence of ethylene traps the benzyne intermediate and generates the hafnacyclopentene Cp*$_2$Hf$CH_2CH_2C_6H_4$.

Introduction

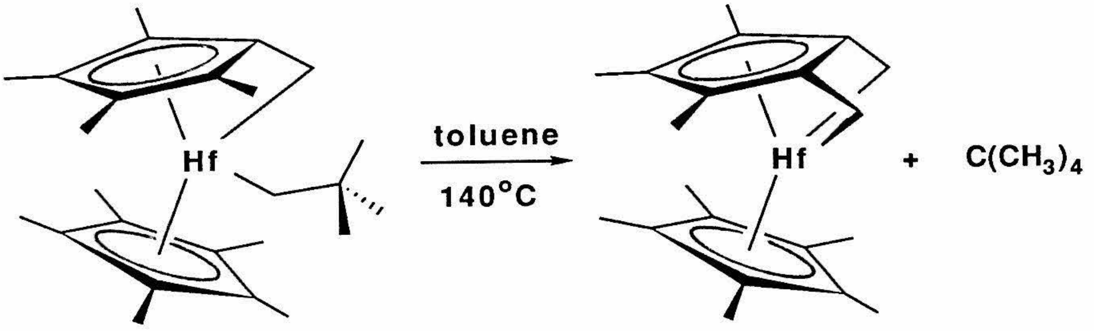
The η^5–pentamethylcyclopentadienyl (Cp*) ligand is widely employed in organometallic chemistry and in general provides a stable ligand environment for reaction chemistry at metal centers. The steric bulk and the absence of activated sp^2 C–H bonds in this ligand has allowed for the formation of stable monomeric metallocene hydride and alkyl derivatives of the early transition metals.[1] It has become recognized, however, that the Cp* ligand is not restricted to being a simple ancillary ligand, but is able to participate in reaction chemistry by metalation of its methyl C–H bonds. Several complexes containing metallated Cp*–containing derivatives have now been isolated. Bercaw and coworkers described the formation of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)TiCH_3$ which is formed upon thermolysis of $Cp^*_2TiMe_2$.[2] The dimeric titanium complex, $[(Cp^*Ti)_2\text{–}\mu\text{–}(\eta^5,\eta^1\text{–}C_5Me_4CH_2)(\mu\text{–}O)_2]$, reported in 1985 by Bottomley, et al., is the first example of a crystallographically characterized compound containing a $\eta^5,\eta^1\text{–}C_5Me_4CH_2$ moeity derived from a Cp* ligand.[3] Additionally, complexes containing metallated pentamethylcyclopentadienyl ligands have been implicated as intermediates in H/D exchange reactions of Cp* ligands[4], in the elimination of isobutane from $Cp^*_2Zr(CH_2CHMe_2)H$[5], in the conversion of $Cp^*_2Hf(CH_2C_6H_5)_2$ to $Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$ and toluene[6], and in the reaction of $Cp^*_2Sc\text{–}CH_3$ with benzene to give methane and $Cp^*_2Sc\text{–}C_6H_5$.[7] In light of the widespread use of pentamethylcyclopentadienyl ligands in transition metal chemistry, a more thorough investigation into its reactivity seems warranted. Herein are described some mechanistic aspects of the synthesis and reactivity of hafnium complexes containing singly or doubly metallated pentamethylcyclopentadienyl ligands.

Results and Discussion

The metallated iodide complex $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)HfI$ (**1**) described in Chapter 1 serves as a convenient starting material for a wide range of mono-metallated permethylhafnocene derivatives of the type $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)Hf\text{-}R$ (R = alkyl or aryl). Treatment of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)HfI$ with neopentyllithium cleanly affords $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)Hf(CH_2CMe_3)$ (**2**) (equation 1).

$$\underset{\mathbf{1}}{Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)HfI} \xrightarrow[-\ Li^+I^-]{+\ LiCH_2CMe_3} \underset{\mathbf{2}}{Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)Hf(CH_2CMe_3)} \qquad (1)$$

Unlike $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)Hf(CH_2C_6H_5)$ (the benzyl analogue of **2**) which undergoes a facile intramolecular rearrangement to $Cp^*_2\overline{HfCH_2\text{-}o\text{-}C}_6H_4$ [6], **2** exhibits considerable thermal stability and decomposes only at elevated temperatures. Toluene solutions of **2** cleanly eliminate neopentane over the course of 1 day at 140° to produce the doubly metallated permethylhafnocene derivative $Cp^*(\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Hf$ (**3**) (equation 2).



2 **3** (2)

Complex **3** can be isolated in moderate yield from cold petroleum ether as air sensitive orange crystals. Teuben et al. have reported that the Ti and Zr analogs of **3** can be prepared in refluxing mesitylene solutions of $(\eta^5\text{-}C_5Me_5)_2M(CH_3)_2$ [8] (conditions in which $(\eta^5\text{-}C_5Me_5)_2Hf(CH_3)_2$ shows no evidence of decomposition after 3-5 days). The tungsten analogue of **3** has been prepared by irradiation of $Cp^*_2WH_2$.[9] That metalation occurs on adjacent methylene groups of the same Cp* ligand in **3** is supported by ^1H and ^{13}C NMR data (Table 1). In order to confirm the unusual structure of $Cp^*(\eta^5,\eta^1,\eta^1\text{–}C_5Me_3(CH_2)_2)Hf$ and because of the scarcity of structural information for metallated pentamethylcyclopentadienyl containing derivatives in general, the X–ray crystal structure determination of **3** was carried out. The molecular configuration of **3** is shown in Figure 1 and a skeletal view is shown in Figure 2.

$Cp^*(\eta^5,\eta^1,\eta^1\text{–}C_5Me_3(CH_2)_2)Hf$ possesses a mirror plane bisecting the two metallated methylene groups. The two methylene fragments are bent 41 ° out of the plane formed by the 5 inner ring carbons of the cyclopentadienyl ligand (Table 3), a value consistent with other structurally characterized transition metal complexes containing fulvene–like ligands.[10] The Hf–C distances for the two metallated methylene groups average 2.346(11) Å, a slight elongation compared to other Hf–C sigma bond distances. For example, distances of 2.280(13) and 2.295(14) Å have been determined for the hafnium–carbon sigma bonds of $Cp^*_2Hf(OO\text{–}^tBu)(CH_2CH_3)$[11] and $[Cp_2HfMe]_2O$[12], respectively. The averaged hafnium–methylene carbon–ring carbon angle (Hf–C(21M)–C(21) and Hf–C(22M)–C(22)) is 65°. Metalation of the two methyl groups also results in the hafnium "sliding forward" within the cyclopentadienyl ring system. The hafnium–ring carbon distances of the metallated Cp* vary from an average of 2.176 Å for the two carbons bearing the methylene groups (Hf–C(21) and Hf–C(22)) to 2.615(8) Å for the most distant ring carbon (Hf–C(24)). An additional consequence of double metalation is the near parallelism of the cyclopentadienyl rings, the dihedral angle between the two planes being only 12(4)°.

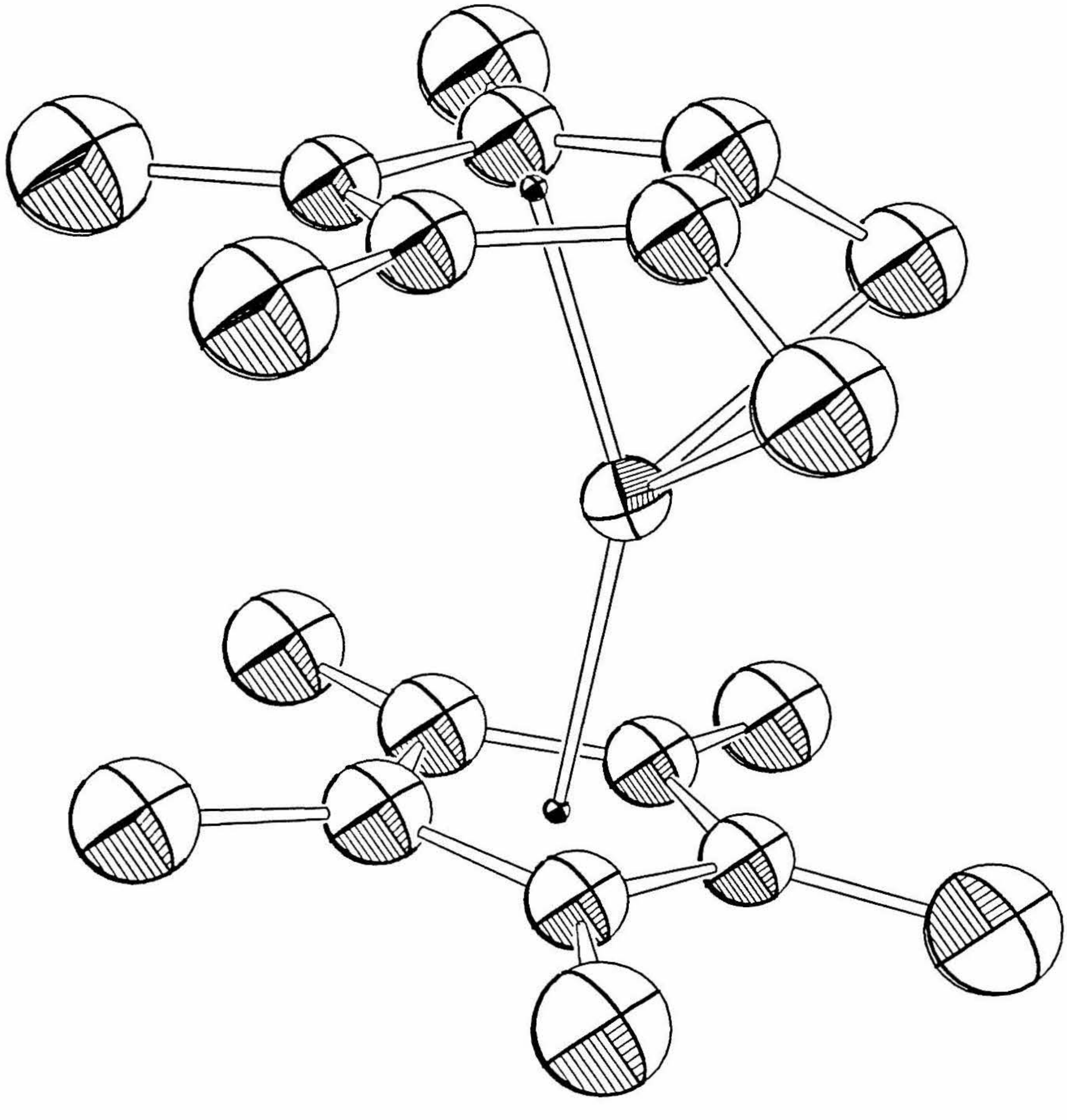


Figure 1. The molecular configuration of Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf. The thermal ellipsoids are shown at the 50% probability level.

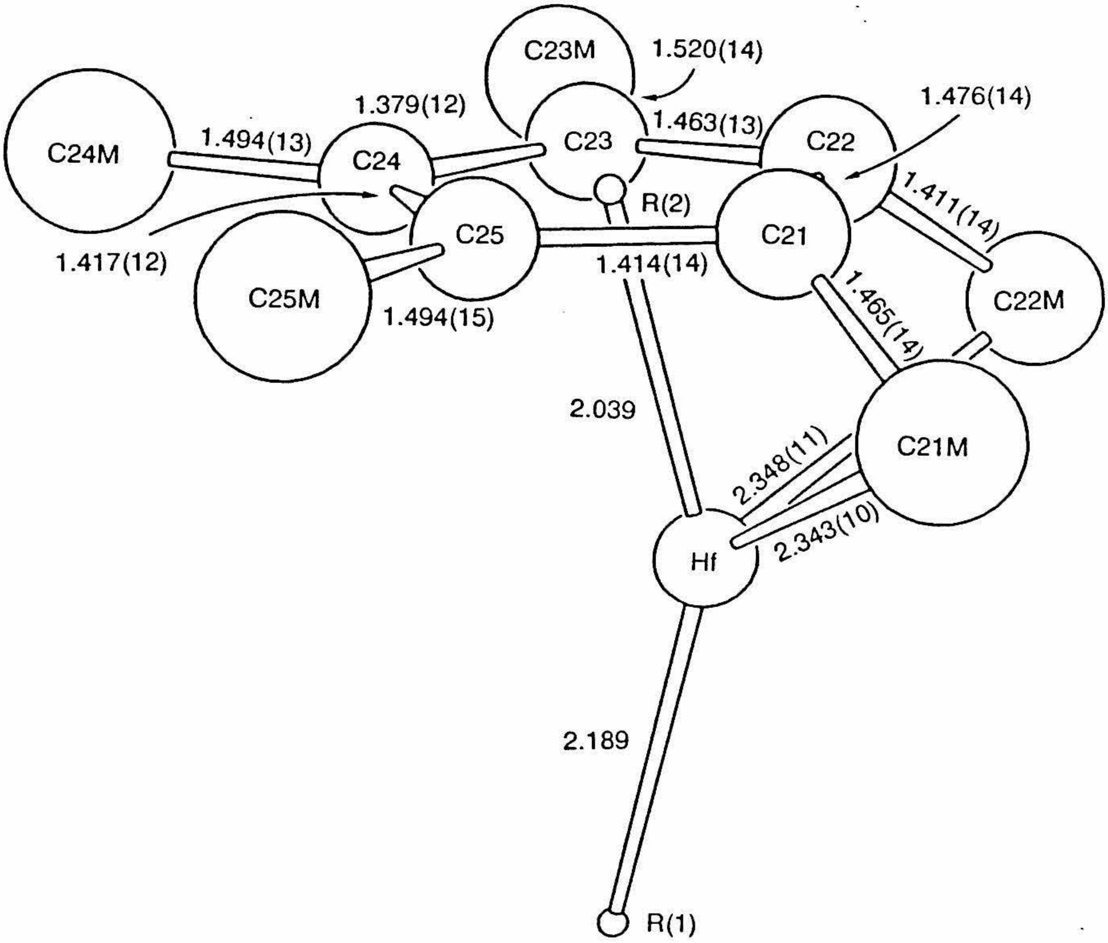
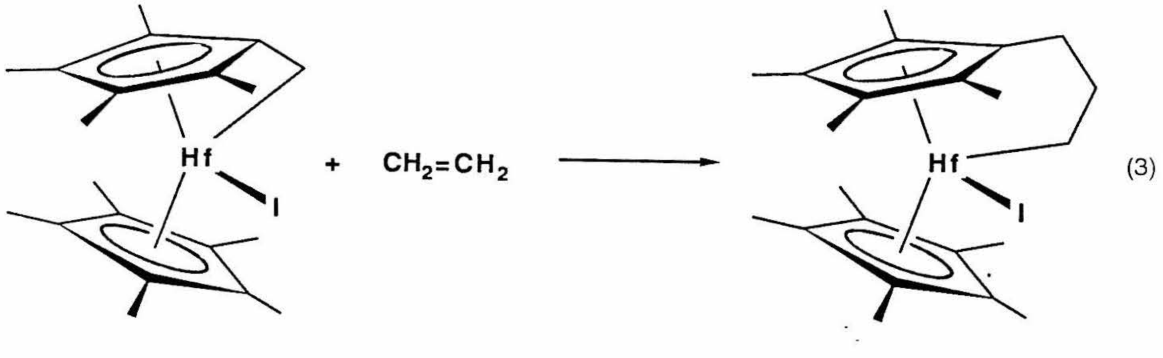


Figure 2. A skeletal view of Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf. The nonmetallated Cp* ligand has been omitted for clarity.

The hafnium–methylene carbon bonds of **1** and **3** exhibit enhanced reactivity as compared to typical permethylhafnocene–alkyl bonds. This heightened reactivity is presumably a consequence of the unusual bond angles and lengths of the metallated methylene groups and the resulting steric accessibility of the hafnium center. Thus, benzene solutions of **1** and **3** react with dihydrogen within seconds to generate the nonmetallated derivatives $(\eta^5\text{–}C_5Me_5)_2Hf(H)I$ and $(\eta^5\text{–}C_5Me_5)_2HfH_2$, respectively. This contrasts with the hydrogenation of $(\eta^5\text{–}C_5Me_5)_2Hf(CH_3)_2$, which requires temperatures of 140° C for several days before generating $(\eta^5\text{–}C_5Me_5)_2HfH_2$ and methane.

The hafnium–methylene bonds of **1** and **3** readily insert one equivalent of ethylene or acetylene. Heating benzene solutions of **1** in the presence of ethylene quantitatively (^{1}H NMR) forms the propyl bridged iodide complex **4** (equation 3).



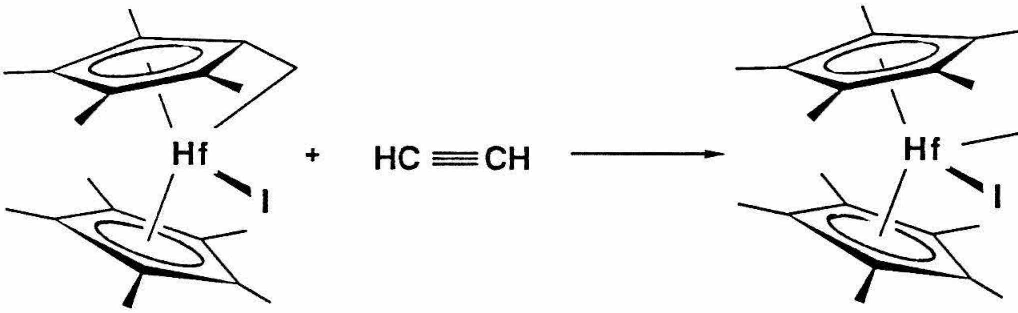
1 **4** (3)

Compound **4** has been characterized by ^{1}H NMR, ^{13}C NMR and microanalytical data. As expected, the ^{1}H and ^{13}C NMR spectra of **4** exhibit four inequivalent methyl resonances for the $(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)$ ligand. Each of the six propyl bridge hydrogens are diastereotopic and give rise to six distinct multiplets in the ^{1}H NMR spectrum. These resonances were not assigned unequivocally to specific hydrogens of the propyl bridge. The proton coupled ^{13}C NMR spectrum of **4** contains three triplets at δ 26.71 ($^1J_{CH}$ = 127 Hz), δ 39.29 ($^1J_{CH}$ = 123 Hz), and δ 70.33 ($^1J_{CH}$ = 127 Hz) which are attributed to the propyl bridge carbons of the (η^5,η^1–$C_5Me_4CH_2CH_2CH_2$) ligand. Complex **4** has been independently prepared by treating Cp*(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)HfH[13] with excess methyl iodide (equation 4).

$$\underset{\mathbf{7}}{\mathrm{Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)HfH}} \xrightarrow[-\ \mathrm{CH_4}]{\mathrm{CH_3I}} \underset{\mathbf{4}}{\mathrm{Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)HfI}} \quad (4)$$

Green and coworkers have utilized alternative methods to prepare tungstenocene and molybdocene derivatives which contain ethyl or butyl linkages between a cyclopentadienyl ligand and the metal center.[14]

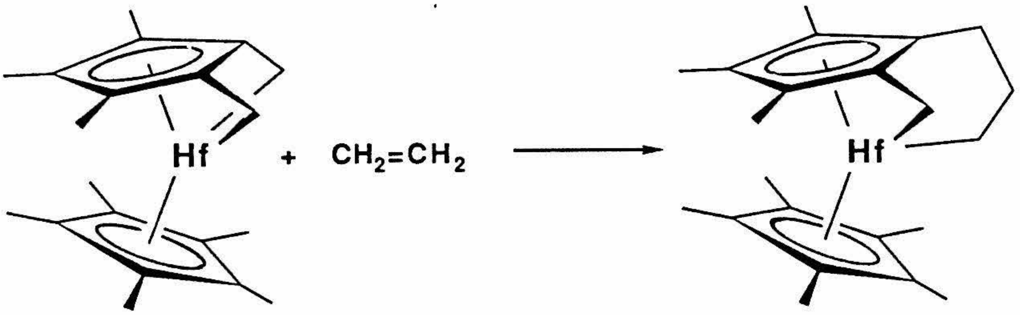
The reaction of the metallated iodide complex **1** with acetylene proceeds in melting benzene to cleanly generate the propylene bridged iodide complex **5** (equation 5). No



1 **5** (5)

metathesis of the acetylene C–H bond with the Hf–C bond of **1** is observed. This lack of reactivity contrasts with that of compounds of the type (η^5–C_5Me_5)$_2$ScR (R = alkyl or H) which undergo sigma bond metathesis with terminal acetylenes to give R–H and permethylscandocene acetylide derivatives.[15]

The doubly metallated complex **3** slowly (2 weeks at 35 °C) incorporates one equivalent of ethylene to form the mixed methylene bridged/propyl bridged species **6** (equation 6).

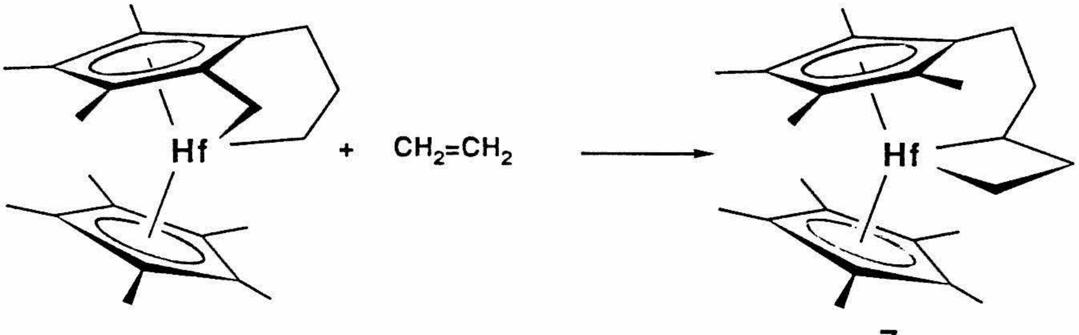


(6)

3

6

The titanium analog Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Ti undergoes a similar insertion of methyl phenyl ketone to yield a titanium alkoxide species.[8] Incorporation of a second equivalent of ethylene is achieved at slightly higher temperatures. An isolated sample of complex **6**



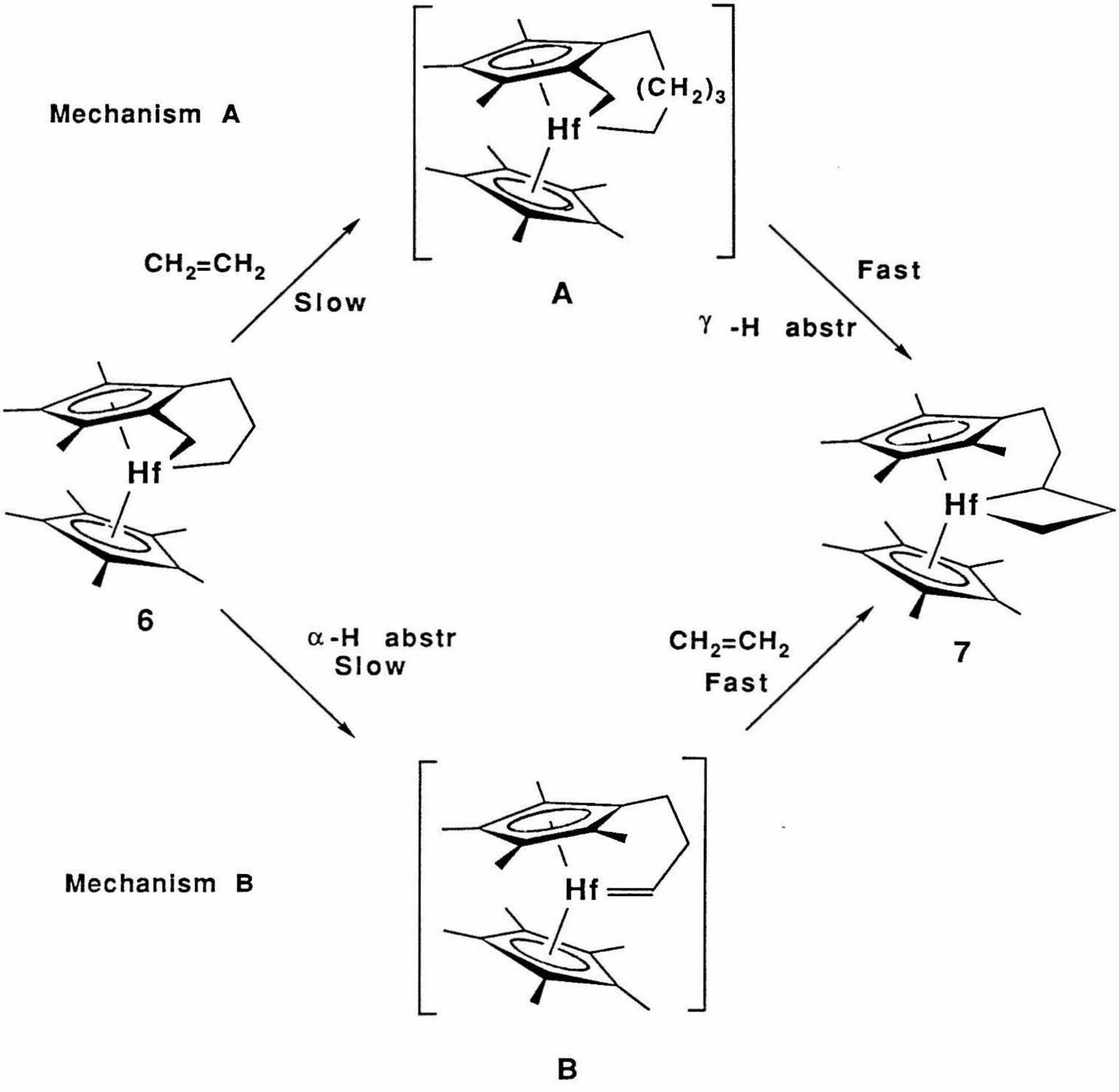
(7)

6

7

(or complex **3**) cleanly generates the novel α–substituted metallacycle **7** (equation 7) when heated in the presence of excess ethylene. The structural assignment of **7** is based on NMR evidence which includes 5 new carbon resonances (4 triplets and 1 doublet) in the ^1H coupled ^{13}C NMR attributed to the 3 metallacycle ring carbons and the 2 carbon bridge linking the cyclopentadienyl ring to an alpha carbon of the metallacyclobutane ring.

Two potential mechanisms for the formation of **7** are outlined in Scheme **1**. Mechanism **A** requires a rate–determining bimolecular insertion of ethylene into the hafnium carbon bond of the propyl bridge of **6** to form a transient pentyl bridged species **A,** followed by a rapid gamma–H abstraction by the adjacent methylene bridge to yield **7.** Thus, mechanism **A** predicts a linear dependence of the reaction rate on the concentration of ethylene. Mechanism **B** involves the initial abstraction of an α–H atom of the propyl bridge by the neighboring methylene group to generate a intermediate alkylidene species **B.** Assuming intermediate **B** can be efficiently trapped by ethylene, a rate independent of the ethylene concentration will be observed. It is found experimentally that the rate of conversion of **6** to metallacycle **7** obeys first order kinetics in the presence of a large excess of ethylene and is independent of the ethylene concentration over the range 0.1 M to 0.4 M ($k = 3.6 \pm 0.1 \times 10^{-6}$ sec^{-1} at 82°C). Additionally, a substantial kinetic deuterium isotope effect is observed when Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)(CH_2CD_2CD_2)$)Hf, **6**–*d*$_4$ (prepared from **3** and ethylene–*d*$_4$), is converted to **7** in the presence of ethylene ($k_H/k_D = 6 \pm 1$ at 82°C). The observation of the kinetic deuterium isotope effect along with the pseudo–first order kinetic behavior for the conversion of **6**–*d*$_4$ to **7**–*d*$_4$ in the presence of C_2H_4 also speaks against a pre–equilibrium involving reversible ethylene elimination from the propyl bridge of **6** to reform the methylene bridge of **3.** Furthermore, the reaction of ^{13}C labeled ethylene with **6** generates metallacycle **7** in which the labeled carbon is incorporated exclusively into the primary α carbon and the β carbon of the metallacyclobutane ring. The data are most consistent with mechanism **B,** i.e., the rate of conversion of **6** to metallacycle **7** is controlled by the abstraction of an α–hydrogen off the propyl bridge by the adjacent methylene group.

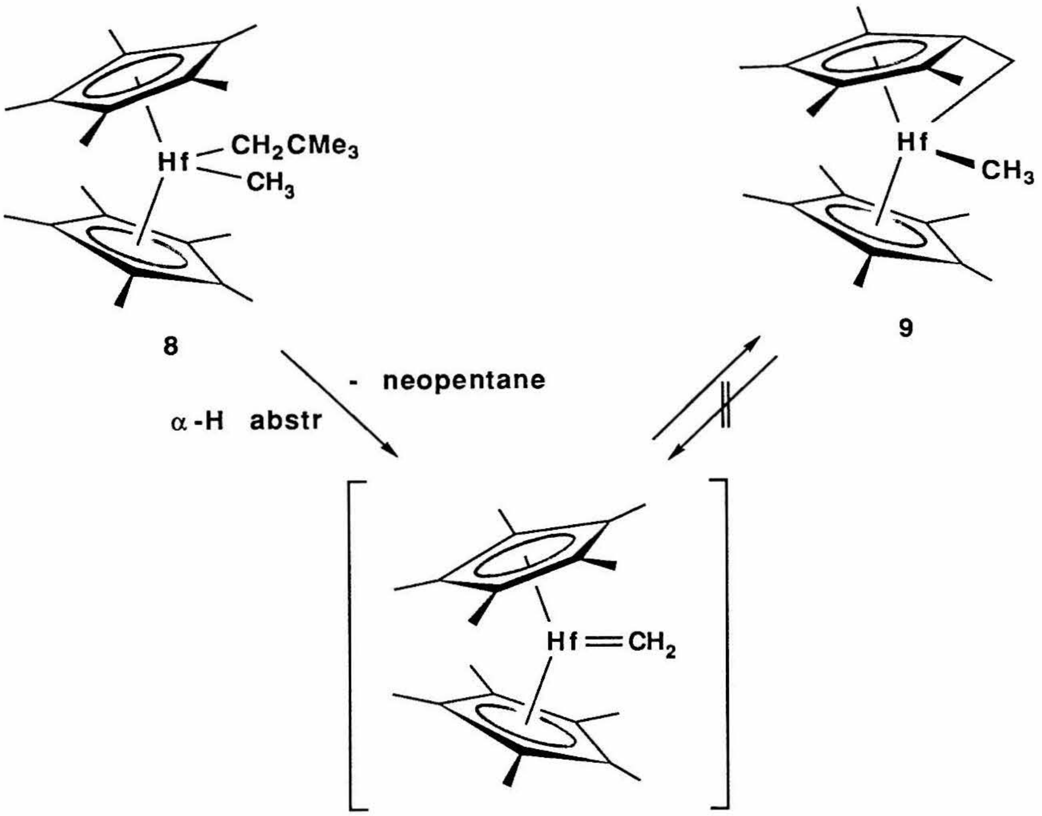


Scheme 1. Two potential mechanisms for the formation of **7** from **6** and ethylene.

It can be demonstrated, however, that the abstraction of an adjacent α–hydrogen by the methylene group of a metallated Cp* ligand is not a general reaction. Thermolysis of the mixed alkyl complex $Cp^*_2Hf(CH_2CMe_3)CH_3$ (**8**) (prepared from $Cp^*_2Hf(CH_2CMe_3)I$ and methyllithium), cleanly generates neopentane and the mono–metallated methyl complex $Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)HfCH_3$ (**9**) (equation 8).

$$\underset{\textbf{8}}{Cp^*_2Hf(CH_2CMe_3)CH_3} \xrightarrow[C_6D_6]{140\,°C} \underset{\textbf{9}}{Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)HfCH_3} + C(CH_3)_4 \qquad (8)$$

Repeating the thermolysis with $Cp^*_2Hf(CH_2CMe_3)CD_3$ (**8**–d_3) (prepared from $Cp^*_2Hf(CH_2CMe_3)I$ and $LiCD_3$) yields **9** and neopentane–d_1 (identified by comparison of its infrared spectra with an authentic sample of neopentane–d_1). The ^1H NMR spectrum of the resulting labeled **9** contains a quartet ($^2J_{DH}$ = 2 Hz) at –1.1 ppm, consistent with the formation of $Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)Hf–CD_2H$ (**9**–d_2). These results suggest that the thermal decomposition of **8** proceeds via an α–hydrogen abstraction of a methyl hydrogen by the adjacent neopentyl ligand to form a transient methylidene complex of permethylhafnocene, followed by the rapid transfer of a ring methyl C–H bond across the hafnium methylidene double bond (Scheme 2). Continued thermolysis (1 day at 140°) of $Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)HfCD_2H$ fails to produce detectable concentrations of $Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)Hf–CH_2D$ or $Cp^*(\eta^5,\eta^1–C_5Me_4CH_2)Hf–CH_3$, suggesting that α–hydrogen abstraction of a methyl group hydrogen (or deuterium) by the adjacent methylene group is not in this case facile (i.e., the metallated methyl derivative is not in equilibrium with the permethylhafnocene methylidene complex).



Scheme 2. Proposed mechanism for the formation of Cp*(η^5,η^1–$C_5Me_4CH_2$)$HfCH_3$ (**9**) from Cp*$_2$Hf(CH_2CMe_3)CH_3 (**8**).

The lack of reactivity shown by the metallated Cp* ligands of complexes derived from permethylhafnocene towards arene solvents, e.g. benzene and toluene, is quite surprising. Indeed, the doubly metallated complex **3** is prepared by the thermolysis of **2** in toluene. Furthermore, the lack of deuterium incorporation into the metallated Cp* ligand of **3** when thermolyzed for 1 week at 140 °C in benzene–*d*$_6$ speaks against reversible solvent activation. In contrast, the metallated permethylscandocene derivative (Cp*(η^5,η^1–$C_5Me_4CH_2$)Sc)$_x$ does react with benzene to form (η^5–C_5Me_5)$_2ScC_6H_5$.[7]

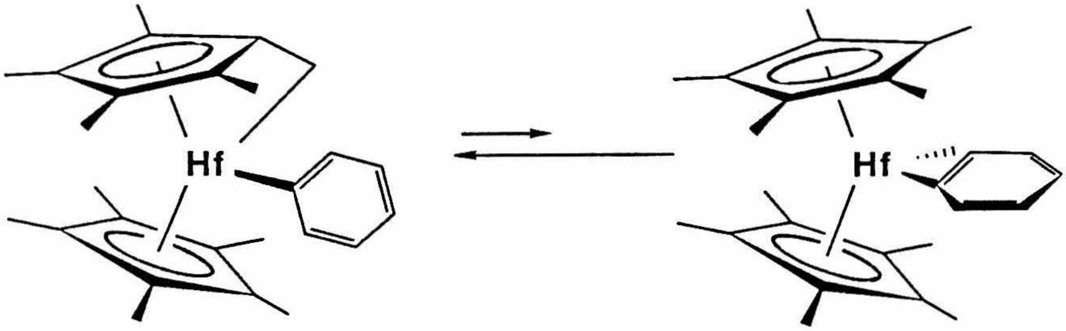
The mono–metallated phenyl derivative Cp*(η^5,η^1–$C_5Me_4CH_2$)HfC_6H_5 (**12**) is synthesized as shown below (equations 9–11).

$$Cp^*{}_2HfI_2 + LiC_6H_5 \longrightarrow \underset{\mathbf{10}}{Cp^*{}_2Hf(C_6H_5)I} + LiI \quad (9)$$

$$\underset{\mathbf{10}}{Cp^*{}_2Hf(C_6H_5)I} + LiCH_3 \longrightarrow \underset{\mathbf{11}}{Cp^*{}_2Hf(C_6H_5)CH_3} + LiI \quad (10)$$

$$\underset{\mathbf{11}}{Cp^*{}_2Hf(C_6H_5)CH_3} \xrightarrow[\Delta]{} \underset{\mathbf{12}}{Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfC_6H_5} + CH_4 \quad (11)$$

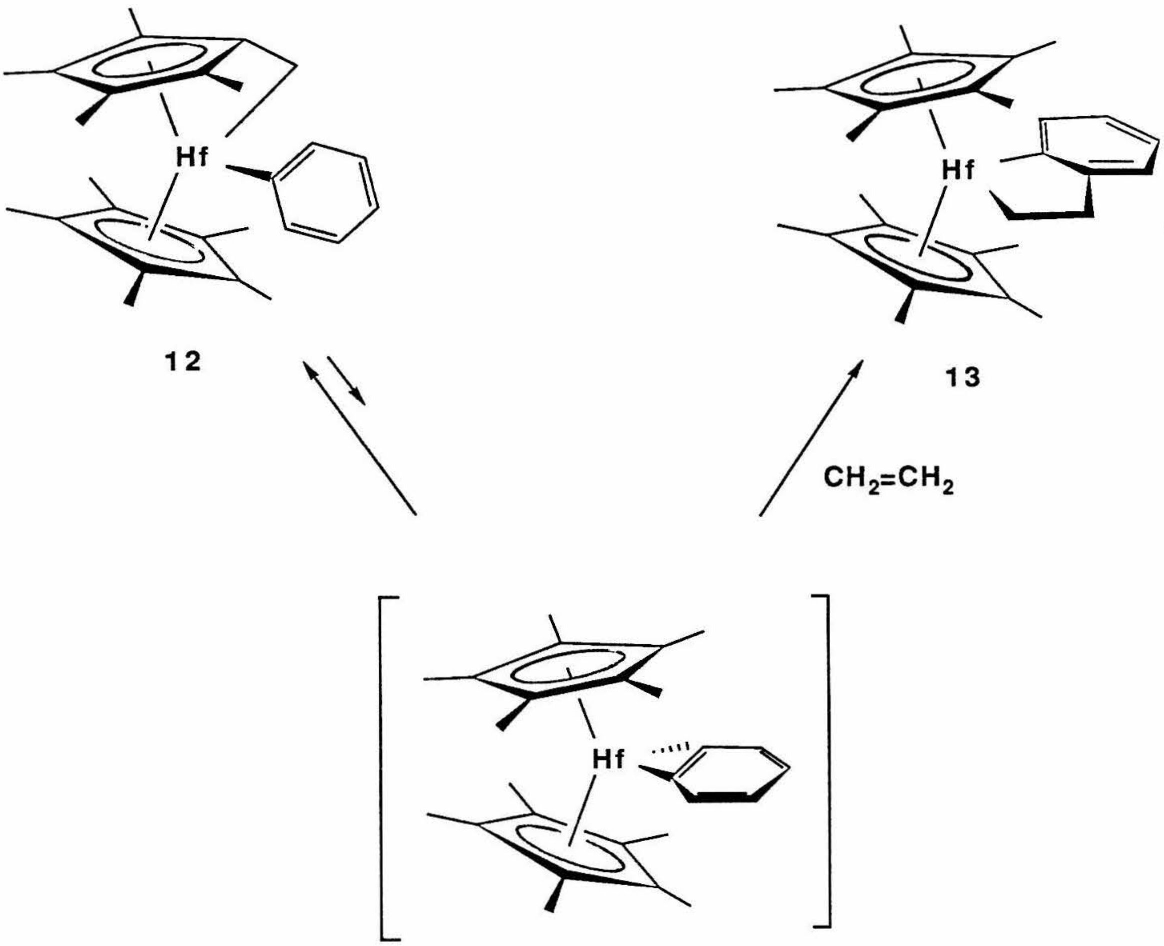
The zirconium analogue of **12**, prepared by the thermal elimination of benzene from $Cp^*{}_2Zr(C_6H_5)_2$, has been recently reported.[16] Complex **12** does not lose benzene or undergo solvent exchange upon prolonged thermolysis (days at 140 C) in benzene–d_6. The methane produced upon thermolysis of the deuterium–labeled complex $Cp^*(\eta^5\text{–}C_5Me_5)Hf(C_6D_5)CH_3$ is exclusively CH_3D (^1H NMR), consistent with the abstraction of an ortho–phenyl hydrogen by the adjacent hafnium–methyl fragment to produce methane and a transient benzyne complex of permethylhafnocene. Rapid addition of a ring methyl hydrogen to this benzyne intermediate would result in the observed metallated phenyl complex. Transient benzyne derivatives of group IV metallocenes have ample precedent in the literature[17] and the trimethylphosphine–stabilized benzyne derivative $Cp_2Zr(\eta^2\text{–}C_6H_4)PMe_3$ has been crystallographically characterized.[18] The remaining deuteriums in **12**–d_4 (derived from the thermolysis of $Cp^*(\eta^5\text{–}C_5Me_5)Hf(C_6D_5)CH_3$ in cyclohexane–d_{12}) do not reside exclusively in the phenyl ligand, but are distributed into all positions of the complex (^2H NMR). This implies the existence of an equilibrium between **12** and the proposed benzyne intermediate $(\eta^5\text{–}C_5Me_5)_2Hf(\eta^2\text{–}C_6H_4)$ (equation 12). Such an equilibrium, combined with rotation about



(12)

12

the Hf–C_{phenyl} bond of **12**, provides a plausible mechanism for the complete exchange of hydrogen positions within the molecule.[19] Furthermore, heating **12** in the presence of ethylene does not result in the formation of a propyl–bridged phenyl complex analogous to $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)HfI$ **4**, but instead quantitatively generates $(\eta^5\text{–}C_5Me_5)_2\overline{Hf(CH_2CH_2C}_6H_4)$ **13**, the product expected from the trapping of $(\eta^5\text{–}C_5Me_5)_2Hf(\eta^2\text{–}C_6H_4)$ with ethylene (Scheme 3).



Scheme 3. Proposed mechanism for the formation of metallacycle **13** from the mono-metallated phenyl derivative **12** and ethylene.

Thus, strong evidence is provided for a reversible hydrogen transfer between the pentamethylcyclopentadienyl ligand of $(\eta^5\text{–}C_5Me_5)_2Hf(\eta^2\text{–}C_6H_4)$ and the ortho–phenyl position of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfC_6H_5$.

Conclusions

In summary, the syntheses and reactivities of singly and doubly metallated pentamethylcyclopentadienyl–containing derivatives of permethylhafnocene have been investigated. Metallation of Cp* ligands has been observed to occur *(i)* directly, via the coupling of a Cp* hydrogen with a hafnium alkyl, *e.g.* the formation of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ (**1**) and neopentane from $Cp^*_2Hf(CH_2CMe_3)I$, or *(ii)* indirectly, by the intramolecular rearrangement of unstable species such as $[Cp^*_2Hf{=}CH_2]$ or $[Cp^*_2Hf(\eta^2\text{–}C_6H_4)]$.

The $Hf\text{–}C_{methylene}$ bonds of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ (**1**) and $Cp^*(\eta^5,\eta^1,\eta^1\text{–}C_5Me_3(CH_2)_2)Hf$ (**3**) exhibit enhanced reactivity towards suitable substrate molecules as compared to typical permethylhafnocene–alkyl bonds. This heightened reactivity is presumably a consequence of the unusual bond angles and lengths of the metallated methylene groups and the resulting steric accessibility of the hafnium center. For example, ethylene readily inserts into the $Hf\text{–}C_{methylene}$ bonds of **1** and **3** to form the propyl–bridged species $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)HfI$ (**4**) and $Cp^*(\eta^5,\eta^1,\eta^1\text{–}C_5Me_3(CH_2)(CH_2CH_2CH_2)Hf$ (**6**), respectively. Compound **6** reacts with a second equivalent of ethylene to form $Cp^*(\eta^5,\eta^1,\eta^1\text{–}C_5Me_4CH_2CH_2\overline{CHCH_2CH_2)Hf}$ (**7**). Kinetic data suggest that this reaction proceeds by a rate determining transfer of an α–hydrogen from the propyl bridge of **6** to the adjacent metallated methylene unit and that the resulting alkylidene species is trapped by ethylene. Intramolecular C–H bond activation is also observed to occur in the mono–metallated phenyl compound $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfC_6H_5$ (**12**), which is in equilibrium with the benzyne adduct $[Cp^*_2Hf(\eta^2\text{–}C_6H_4)]$. This benzyne adduct is trapped by ethylene to form $Cp^*_2\overline{HfCH_2CH_2C}_6H_4$. In the absence of suitable substrates, however, metallated derivatives of permethylhafnocene exhibit remarkable thermal stability. Thus, benzene solutions of **1** or **3** are unchanged after two weeks at 140°C.

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

Compound	Assignment	δ (ppm)	Coupling^b
$Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)HfCH_2CMe_3$ (2)			
	$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.93 s	
	$\eta^5,\eta^1\text{-}C_5Me_4C\mathit{H}_2$	1.53 d	$^2J_{HH} = 7.5$
		1.83 d	$^2J_{HH} = 7.5$
	$\eta^5,\eta^1\text{-}C_5(C\mathit{H}_3)_4CH_2$	1.58 s	
		1.75 s	
		1.98 s	
		2.17 s	
	$Hf\text{–}C\mathit{H}_2C(CH_3)_3$	−1.58 d	$^2J_{HH} = 13$
		0.37 d	$^2J_{HH} = 13$
	$Hf\text{–}CH_2C(C\mathit{H}_3)_3$	1.13 s	
$Cp^*(\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Hf$ (3)			
	$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.90 s	
	$\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(C\mathit{H}_2)_2$	0.93 d	$^2J_{HH} = 7$
		0.73 d	$^2J_{HH} = 7$
	$\eta^5,\eta^1,\eta^1\text{-}C_5(C\mathit{H}_3)_3(CH_2)_2$	1.46 s (2 methyls)	
		1.41 s (1 methyl)	
	$\eta^5\text{-}\mathit{C}_5(CH_3)_5$	118.4 s	
	$\eta^5\text{-}C_5(\mathit{C}H_3)_5$	12.00 q	$^1J_{CH} = 126$
	$\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(\mathit{C}H_2)_2$	62.25 t	$^1J_{CH} = 145$
$Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2CH_2CH_2)HfI$ (4)			
	$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.91 s	
	$\eta^5,\eta^1\text{-}C_5Me_4C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$	-0.72 m	
		0.67 m	
		1.97 m	
		2.28 m	
		2.65 m	
		2.97 m	
	$\eta^5,\eta^1\text{-}C_5(C\mathit{H}_3)_4CH_2CH_2CH_2$	1.56 s	
		1.61 s	
		1.73 s	
		2.84 s	
	$\eta^5\text{-}\mathit{C}_5(CH_3)_5$	119.08 s	
	$\eta^5\text{-}C_5(\mathit{C}H_3)_5$	13.36 q	$^1J_{CH} = 123$
	$\eta^5,\eta^1\text{-}C_5Me_4CH_2CH_2\mathit{C}H_2$	70.33 t	$^1J_{CH} = 127$
	$\eta^5,\eta^1\text{-}C_5Me_4CH_2\mathit{C}H_2CH_2$	39.29 t	$^1J_{CH} = 123$
	$\eta^5,\eta^1\text{-}C_5Me_4\mathit{C}H_2CH_2CH_2$	26.71 t	$^1J_{CH} = 127$
	$\eta^5,\eta^1\text{-}C_5(\mathit{C}H_3)_4CH_2CH_2CH_2$	11.38 q	$^1J_{CH} = 125$
		12.24 q	$^1J_{CH} = 125$
		15.14 q	$^1J_{CH} = 125$
		17.84 q	$^1J_{CH} = 127$

$Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2CH{=}CH)HfI$ (5)

$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.92 s	
$\eta^5,\eta^1\text{–}C_5(C\mathit{H}_3)_4CH_2CH{=}CH$	1.70 s	
	1.78 s	
	1.82 s	
	2.68 s	
$\eta^5,\eta^1\text{–}C_5Me_4CH_2CH{=}C\mathit{H}$	7.09 dt	$^3J_{HH}$ = 12, 2
$\eta^5,\eta^1\text{–}C_5Me_4CH_2C\mathit{H}{=}CH$	7.88 dt	$^3J_{HH}$ = 12, 3
$\eta^5,\eta^1\text{–}C_5Me_4C\mathit{H}_2CH{=}CH$	2.78 m	

$Cp^*(\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)(CH_2CH_2CH_2))Hf$ (6)

$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.81 s	
$\eta^5,\eta^1,\eta^1\text{–}C_5(C\mathit{H}_3)_3(CH_2)(CH_2CH_2CH_2)$	1.38 s	
	1.62 s	
	1.91 s	
$\eta^5,\eta^1,\eta^1\text{–}C_5Me_3(C\mathit{H}_2)(CH_2CH_2CH_2)$	1.51 d	$^2J_{HH}$ = 8
	1.86 d	$^2J_{HH}$ = 8
$\eta^5,\eta^1,\eta^1\text{–}C_5Me_3(CH_2)(C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2)$	–0.96 m	
	–0.04 m	
	1.86 m	
	2.40 m	
	2.47 m	
	2.66 m	
$\eta^5\text{-}C_5(\mathit{C}H_3)_5$	11.73 q	$^1J_{CH}$ = 126
$\eta^5\text{-}\mathit{C}_5(CH_3)_5$	116.3 s	
$\eta^5,\eta^1,\eta^1\text{–}C_5(CH_3)_3(\mathit{C}H_2)(CH_2CH_2CH_2)$	68.40 t	$^1J_{CH}$ = 142
$\eta^5,\eta^1,\eta^1\text{–}C_5(CH_3)_3(CH_2)(\mathit{C}H_2CH_2\mathit{C}H_2)$	29.60 br, t	$^1J_{CH}$ = 123
	35.83 br, t	$^1J_{CH}$ = 123
	66.73 m	

$Cp^*Hf(\eta^5,\eta^1,\eta^1\text{-}C_5Me_4(CH_2CH_2CHCH_2CH_2))$ (7)

$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.80 s	
$\eta^5,\eta^1,\eta^1\text{–}C_5(C\mathit{H}_3)_4(CH_2CH_2CHCH_2CH_2)$	1.53 s	
	1.63 s	
	1.74 s	
	2.40 s	
$\eta^5,\eta^1,\eta^1\text{–}C_5Me_4(CH_2CH_2CHCH_2C\mathit{H}_2)$	–0.81 m	
	1.12 m	
$\eta^5,\eta^1,\eta^1\text{–}C_5Me_4(CH_2CH_2CHC\mathit{H}_2CH_2)$	2.33 m	
	2.60 m	
$\eta^5,\eta^1,\eta^1\text{–}C_5Me_4(CH_2CH_2C\mathit{H}CH_2CH_2)$	3.03 m	
$\eta^5,\eta^1,\eta^1\text{–}C_5Me_4(CH_2C\mathit{H}_2CHCH_2CH_2)$	–0.40 m	
	0.79 m	
$\eta^5,\eta^1,\eta^1\text{–}C_5Me_4(C\mathit{H}_2CH_2CHCH_2CH_2)$	2.93 m	
	2.97 m	
$\eta^5\text{-}C_5(\mathit{C}H_3)_5$	11.57 q	$^1J_{CH}$ = 125
$\eta^5\text{-}\mathit{C}_5(CH_3)_5$	116.3 s	
$\eta^5,\eta^1,\eta^1\text{–}C_5(\mathit{C}H_3)_4(CH_2CH_2CHCH_2CH_2)$	10.11 q	$^1J_{CH}$ = 125
	11.79 q	$^1J_{CH}$ = 126
	12.63 q	$^1J_{CH}$ = 126

	14.16 q	${}^1J_{CH} = 125$
$\eta^5,\eta^1,\eta^1\mathrm{-C_5Me_4CH_2CH_2CHCH_2}\mathit{C}\mathrm{H_2}$	49.16 t	${}^1J_{CH} = 120$
$\eta^5,\eta^1,\eta^1\mathrm{-C_5Me_4CH_2CH_2CH}\mathit{C}\mathrm{H_2CH_2}$	36.48 t	${}^1J_{CH} = 128$
$\eta^5,\eta^1,\eta^1\mathrm{-C_5Me_4CH_2CH_2}\mathit{C}\mathrm{HCH_2CH_2}$	38.55 d	${}^1J_{CH} = 129$
$\eta^5,\eta^1,\eta^1\mathrm{-C_5Me_4CH_2}\mathit{C}\mathrm{H_2CHCH_2CH_2}$	33.42 t	${}^1J_{CH} = 125$
$\eta^5,\eta^1,\eta^1\mathrm{-C_5Me_4}\mathit{C}\mathrm{H_2CH_2CHCH_2CH_2}$	63.11 t	${}^1J_{CH} = 122$

$\mathbf{Cp^*_2Hf(CH_2CMe_3)CH_3}$ (8)

$\eta^5\mathrm{-C_5(C}\mathit{H}\mathrm{_3)_5}$	1.83 s
$\mathrm{Hf\text{-}C}\mathit{H}\mathrm{_3}$	-0.58 br, s
$\mathrm{Hf\text{-}C}\mathit{H}\mathrm{_2C(CH_3)_3}$	-0.17 br, s
$\mathrm{Hf\text{-}CH_2C(C}\mathit{H}\mathrm{_3)_3}$	1.09 s

$\mathbf{Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)HfCH_3}$ (9)

$\eta^5\mathrm{-C_5(C}\mathit{H}\mathrm{_3)_5}$	1.84 s	
$\eta^5,\eta^1\mathrm{-C_5(C}\mathit{H}\mathrm{_3)_4CH_2}$	1.54 s	
	1.67 s	
	1.73 s	
	1.81 s	
$\eta^5,\eta^1\mathrm{-C_5Me_4C}\mathit{H}\mathrm{_2}$	1.41 d	${}^2J_{HH} =7.7$
	1.86 d	${}^2J_{HH} =7.7$
$\mathrm{Hf{-}C}\mathit{H}\mathrm{_3}$	-1.07 br, s	

$\mathbf{Cp^*_2Hf(C_6H_5)I}$ (10)

$\eta^5\mathrm{-C_5(C}\mathit{H}\mathrm{_3)_5}$	1.83 s
$\mathrm{Hf\text{-}C_6}\mathit{H}\mathrm{_5}$	7.40 m

$\mathbf{Cp^*_2Hf(C_6H_5)CH_3}$ (11)

$\eta^5\mathrm{-C_5(C}\mathit{H}\mathrm{_3)_5}$	1.73 s
$\mathrm{Hf\text{-}C}\mathit{H}\mathrm{_3}$	-0.20 s
$\mathrm{Hf\text{-}C_6}\mathit{H}\mathrm{_5}$	6.7-7.2 m

$\mathbf{Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)HfC_6H_5}$ (12)

$\eta^5\mathrm{-C_5(C}\mathit{H}\mathrm{_3)_5}$	1.74 s	
$\eta^5,\eta^1\mathrm{-C_5Me_4C}\mathit{H}\mathrm{_2}$	1.97 d	${}^2J_{HH} =9$
	1.76 d	${}^2J_{HH} =9$
$\eta^5,\eta^1\mathrm{-C_5(C}\mathit{H}\mathrm{_3)_4CH_2}$	1.74 s	
	1.74 s	
	1.57 s	
	1.20 s	
$\mathrm{Hf{-}C_6}\mathit{H}\mathrm{_5}$	6.3–7.2 m	
$\eta^5,\eta^1\mathrm{-C_5Me_4}\mathit{C}\mathrm{H_2}$	70.51 t	${}^1J_{CH} = 141$

$Cp^*_2Hf(C_6H_5)_2$			
	η^5-$C_5(C\mathit{H}_3)_5$	1.62 s	
	Hf-$C_6\mathit{H}_5$	6.9–7.8 m	
$Cp^*_2\overline{Hf(CH_2CH_2C}_6H_4)$ (13)			
	η^5-$C_5(C\mathit{H}_3)_5$	1.71 s	
	Hf–$C\mathit{H}_2CH_2C_6H_4$	0.73 t	$^3J_{HH} = 8$
	Hf–$CH_2C\mathit{H}_2C_6H_4$	3.23 t	$^3J_{HH} = 8$
	Hf–$CH_2CH_2C_6\mathit{H}_4$	6.6–7.1 m	

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[a] All NMR spectra were recorded in benzene–d_6 and are referenced to internal tetramethylsilane.

[b] Coupling constants are reported in hertz.

Note: The following abbreviations are used to denote the multiplicity of the NMR signals: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Experimental Details.

General Considerations. All manipulations were performed using glovebox, high–vacuum[20] or Schlenk techniques. Solvents were purified by distillation from an appropriate drying agent under a N_2 atmosphere and either used immediately or vacuum transferred from "titanocene" or sodium-benzophenone. Benzene–d_6 was purified by vacuum transfer from activated molecular sieves (4 Å, Linde) and then from "titanocene". ^{1}H and ^{13}C NMR spectra were recorded on Varian EM–390 (90 MHz, ^{1}H), JEOL GX400Q (400 MHz, ^{1}H; 100 MHz, ^{13}C) and Brucker WM500 (500 MHz, ^{1}H) spectrometers. Elemental analyses were performed by Mr. Larry Henling of the CIT Analytical Laboratory.

X–ray Structure Determination of Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)_2$)Hf. Crystal data: monoclinic, space group P2/c, a = 13.775(4)Å, b = 9.516(1)Å, c = 14.183(6)Å, β = 103.965(31)°, V = 1804.0(9)Å^3, Z = 4. A single crystal was used for the photographic workup and data collection; a hemisphere (+h, $\pm k$, $\pm l$) of data was collected (θ scan width 1.2° plus dispersion, θ–2θ scans) at *ca.* 4° (θ)/min to 2θ = 45° on an Enraf–Nonius CAD4 diffractometer with graphite monochromator and MoKα (λ = 0.7107 Å) radiation (5054 reflections, *ca.* 50 hours). The three check reflections showed no unusual decrease in intensity. The data were reduced to F_o^2 and averaged over 2/m symmetry yielding 2360 reflections. The position of Hf(1) was derived from the Patterson map, and the remaining structure was revealed by electron density maps. Hydrogen atoms were located on difference Fourier maps, and were not refined. Full–matrix least–squares refinement of scale factor, atom coordinates and anisotropic Gaussian parameters resulted in a goodness–of–fit $S = \{\Sigma w[F_o^2-(F_c/k)^2]^2/(n-v)\}^{1/2} = 5.53$ (n = 2360 reflections, v = 190 parameters), $R_F = \Sigma||F_o|-|F_c||\Sigma|F_o| = 0.085$ (2276 reflections, $I > 0$), and $R'_F = 0.079$ (1984 reflections, $I > 3\sigma I$); each shift/error < 0.01 in the final cycle.

At this stage, a large peak, *ca.* 10 e/Å^3, was found on the difference Fourier map at coordinates (0.27, 0.29, 0.54), or roughly (1/2–x, 1/2–y, 1–z) where (x,y,z) corresponds to the coordinates of Hf(1); the remaining peaks in the map, remote from the Hf atoms, were less than 1 e/Å^3. Hf(1) was assigned a partial population of p, and a second Hf atom, Hf(2), was added to the refinement with a partial population 1–p. Two cycles of full–matrix least–squares refinement resulted in reasonable U_{ij}'s for both Hf atoms and a refinement gave S = 2.66 (v = 200 parameters), R_F = 0.042, and R'_F = 0.036. The final difference Fourier map indicated peaks and valleys of height *ca.* 2 e/Å^3 around the Hf atoms (as before, presumably residuals from absorption errors), and the remainder of the map was relatively flat with peaks no greater than *ca.* 1 e/Å^3.

Apparently the structure is disordered: about 7% of the time the molecule occupies a different position (the Hf(1)–Hf(2) distance is only 1.26Å) and, presumably, a different orientation as well, which we cannot deduce because of the small scattering power of the fractional carbon atoms. We can construct no sensible twinning model to explain the phenomenon. In any event, the dramatic decreases in S and R_F are ample reason for introducing Hf(2), and we are confident that the omission of the remaining 7.3% carbon and hydrogen atoms of the second molecule has not led to significant errors in the description of the molecular structure.

Kinetics of the reaction of Cp*(η^5,η^1,η^1–$C_5Me_3(CH_2)(CH_2CH_2CH_2)$Hf ,6, with ethylene. Compound **6** (28 mg, 0.059 mmol) and $FeCp_2$ (*ca.* 5 mg) were dissolved in 2.83 g of benzene–d_6. Five NMR tubes were prepared from this stock solution. Varying amounts of ethylene were subsequently added to each tube, with the concentrations ranging from 0.1 M to 0.4 M at 25 °C, and the tubes were sealed. The reactions were followed by monitoring the decrease in intensity of the methyl resonance of **6** at δ 1.38 relative to internal Cp_2Fe. NMR spectra were recorded at timed intervals using a Varian EM–390 (90 MHz) spectrometer. Peak heights were demonstrated to be reproducible to within ± 7% by repeated measurement. Each spectrum was recorded 3 times and the averaged peak height was used to calculate the rate constant. The reaction temperature of 82 °C was maintained using a constant temperature oil bath controlled by thermoregulators and was observed to be constant to within ± 1°C.

Synthetic Procedures:

$Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)Hf(CH_2CMe_3)$ (2). Approximately 20 mL of benzene was condensed into a flask charged with **1** (0.60 g, 1.03 mmol) and $LiCH_2C(CH_3)_3$ (0.09 g, 1.15 mmol). The solution was stirred for 2 hours, then filtered. The solvent was replaced with petroleum ether (*ca.* 5 mL) and the suspension was cooled to −78° C. Filtering gave 0.23 g, (43%) of **2** as a pale orange solid. Elemental analysis: Found(calculated) %C 56.03 (57.85), %H 7.58 (7.73).

$Cp^*(\eta^5,\eta^1,\eta^1-C_5Me_3(CH_2)_2)Hf$ (3). To a thick walled glass bomb was added **2** (0.68 g, 1.3 mmol) and 30 mL of toluene. This solution was stirred for 2 days at 140°C then transferred to a frit assembly in the glove box. The toluene was replaced with petroleum ether and the resulting suspension was cooled to −78° C. Filtering yielded 0.37 g (64%) of **3** as an orange crystalline solid. Elemental analysis: Found(calculated) %C 53.95 (53.78), %H 6.32 (6.27).

$Cp^*(\eta^5,\eta^1-C_5Me_4CH_2CH_2CH_2)HfI$ (4). Method (a) Approximately 20 mL of C_6H_6 was condensed into a small glass bomb containing **1** (1.06 g, 1.8 mmol) and *ca.* 5 equivalents of ethylene. After heating this solution overnight at 110° C. the volatiles were removed *in vacuo.* The resulting solid was transferred to a frit assembly, suspended in *ca.* 10 mL of petroleum ether, cooled to −78° C and filtered. This procedure affords 0.77 g (71%) of **4** as a bright yellow solid. Elemental analysis: Found(calculated) %C 42.55 (43.83), %H 5.36 (5.52). **Method (b)** Iodide **4** can also be prepared by treating benzene solutions of $Cp^*(\eta^5,\eta^1-C_5Me_4CH_2)HfH$ (see chapter 3) with CH_3I to give product and methane.

$Cp^*(\eta^5,\eta^1-C_5Me_4(CH_2CH{=}CH)HfI$ (5). Approximately 5 equivalents of *acetylene* was condensed into a −78° C petroleum ether solution of **1** (0.78 g, 1.36 mmol). This solution was allowed to warm with stirring. The volume of petroleum ether was reduced to 5 mL and the solution was cooled to –78°C. Filtering afforded 0.49 g (60%) of **5** as a pale orange solid. Elemental analysis: Found(calculated) %C 43.96 (43.98), %H 5.19 (5.20).

$Cp^*(\eta^5,\eta^1,\eta^1\text{–}C_5Me_3(CH_2)(CH_2CH_2CH_2)Hf$ (6). A small glass bomb was charged with **3** (0.25 g, 0.56 mmol), *ca.* 10 mL of benzene and 5 equivalents of ethylene. After heating this solution for 12 days at 35°C the volatiles were removed *in vacuo*. The crude product was taken into the glove box and washed with petroleum ether into a frit apparatus. Cooling to –78°C caused the precipitation of **6** as a yellow solid which collected by filtration in *ca.* 40% yield. Elemental analysis: Found(calculated) %C 55.35 (55.63), %H 6.95 (6.79).

$Cp^*Hf(\eta^5,\eta^1,\eta^1\text{–}C_5Me_4CH_2CH_2CHCH_2CH_2)$ (7). A small glass bomb was charged with **3** (0.60 g, 1.34 mol), *ca.* 10 mL of benzene and 10 equivalents of ethylene. This solution was heated overnight at 110°C after which the volatiles were removed *in vacuo*. The crude solid was transferred to a frit assembly and *ca.* 10 mL petroleum ether was added. After filtration the solution was cooled to –78° C. The off–white precipitate was collected by filtration in *ca.* 40% yield. Elemental analysis: Found(calculated) %C 56.94 (57.30), %H 6.97 (7.21).

$Cp^*_2Hf(CH_2CMe_3)CH_3$ (8). To a solution of $Cp^*_2Hf(CH_2CMe_3)I$[22] (0.51 g, 0.79 mmol) and N,N,N',N'–tetramethylethylenediamine (TMEDA) (1.5 mmol) in 20 mL benzene was syringed MeLi/diethyl ether (0.87 mmol). After stirring overnight the benzene was replaced with 20 mL of petroleum ether and the solution was filtered. The solvent volume was reduced to *ca.* 5 mL and cooled to –78⁰ C. Filtration yielded 0.23 g of white **8** (53%).

$Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_3$ (9). Compound **8** (0.46 g, 0.86 mmol) in 5 mL of toluene was heated in a glass bomb overnight at 135⁰ C. The solution was transferred to a sublimator and the solvent was removed *in vacuo*. Subliming at 110⁰ C for 2 days yielded 0.14 g (35%) of yellow **9**. Elemental analysis: Found(calculated) %C 54.88 (54.48), %H 6.63 (6.97).

$Cp^*{}_2Hf(C_6H_5)I$ (10). To $Cp^*{}_2HfI_2$ (1.97 g, 2.79 mmol) in *ca.* 20 mL benzene was syringed a 2–fold excess of LiC_6H_5 in cyclohexane/diethyl ether. After stirring overnight the solvent was replaced with *ca.* 50 mL of petroleum ether and the solution was filtered. The solvent volume was reduced, then cooled to –78° C. Filtration yielded 1.28 g (70%) of cream colored **10.**

$Cp^*{}_2Hf(C_6H_5)CH_3$ (11). To **10** (0.49 g, 0.75 mmol) and TMEDA (*ca.* 1 mmol) in diethyl ether was syringed MeLi/diethyl ether (1.35 mmol). After stirring overnight the diethyl ether was replaced with *ca.* 20 mL of petroleum ether and the solution was filtered. The solvent volume was reduced and cooled to –78⁰ C. Filtration yielded 0.21 g (52%) of white **11.** Elemental analysis: Found(calculated) %C 57.86 (59.93), %H 6.94 (7.08).

$Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfC_6H_5$ (12). Compound **11** (0.60 g, 1.1 mmol) in 5 mL of toluene was heated in a small glass bomb for three days at 135° C. The toluene was replaced with petroleum ether and the solution was transferred to a frit assembly. The solvent volume was reduced and cooled to –78⁰C. Filtering yielded 0.34 g (58%) of yellow **12.**

$(\eta^5\text{–}C_5Me_5)_2Hf(C_6H_5)_2$. $Cp^*{}_2HfI_2$ (1.49 g, 2.1 mmol), excess C_6H_5Li, and 1 mL of TMEDA were stirred in *ca.* 20 mLs of C_6H_6 overnight. The benzene was replaced with petroleum ether and the solution was filtered. Cooling to –78 °C and filtering afforded 0.70 g (55 %) of colorless $(\eta^5\text{–}C_5Me_5)_2Hf(C_6H_5)_2$.

$(\eta^5\text{–}C_5Me_5)_2\overline{Hf(CH_2CH_2C}_6H_4)$ (13). Method (a). A sample of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfC_6H_5$ (**12**) and *ca.* 0.5 mLs of benzene–d_6 were sealed in an NMR tube with excess ethylene. Heating the NMR tube overnight at 130 °C cleanly generated metallacycle **13. Method (b).** A benzene solution of $Cp^*{}_2Hf(C_6H_5)_2$ (0.60 g, 1.0 mmol) and excess ethylene were heated for 2 days at 120 °C. The solution was filtered and the benzene was replaced with petroleum ether. Cooling to –78 °C and filtering afforded 0.2 g

(36%) of off–white **13**. Elemental analysis: Found(calculated) %C 58.14 (60.80), %H 7.08 (6.92).

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(20) It is interesting to note that the previously mentioned zirconium analogue, $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)ZrC_6H_5$ exchanges only the *ortho* phenyl hydrogens with the Cp* ring hydrogens, presumably due to restricted rotation about the zirconium phenyl bond (reference 17). An estimate for the barrier to phenyl rotation in $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfC_6H_5$ is provided from $Cp^*_2Hf(CH_3)(C_6H_4\text{–}m\text{–}CH_3)$, which exists as a 1:1 mixture of the *exo* and *endo* isomers. Data obtained from the coalesence of the *endo* and *exo* Hf–CH_3 resonances suggests $\Delta G^{\ddagger}$ for phenyl rotation is *ca.* 20 kcal·mol^{-1} at 100°C.

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Chapter 3

The Synthesis of Metalation–Resistant Bis(cyclopentadienyl) Ligand Systems. The Molecular Structure of $[(\mu\text{–}Me_2Si)_2(\eta^5\text{–}C_5H_2\text{–}4\text{–}CMe_3)_2]ZrCl_2$.

Introduction

The tendency for pentamethylcyclopentadienyl ligands of early transition metal hydride and alkyl derivatives to undergo intramolecular metalation is well documented.[1] Relatively facile decomposition pathways of this type may preclude the observation and study of other desirable transformations. For this reason, the synthesis of metalation–resistent bis(cyclopentadienyl) ligand systems has been undertaken. At least two methods of increasing the resistance of alkylated cyclopentadienyl ligands towards metalation can be imagined. One method would be to synthesize cyclopentadienyl ligands which contain alkyl groups with extremely strong C–H bonds. In view of the facility with which early transition metal complexes activate the relatively strong sp^2 and sp hybridized C–H bonds of arenes and terminal alkynes[2], we considered this approach unlikely to succeed. The approach we chose to pursue would restrain the alkyl substituents from approaching the empty, low–lying orbitals in the equatorial plane between the cyclopentadienyl rings.[3] It is typically assumed that the activation of substrate molecules requires an initial interaction with these metal–based orbitals. Restraining the pendant cyclopentadienyl alkyl groups from interacting with these orbitals, and hence, from undergoing metalation, would be accomplished by tethering together the cyclopentadienyl rings with two bridges at adjacent carbons and placing a bulky alkyl substituent in the position *"meta"* to both bridges. The presence of two adjacent links between the cyclopentadienyl rings should severely restrict the rotation of the cyclopentadienyl ligands and make the conformation necessary for intramolecular metalation less favorable. The preliminary results of these efforts are reported herein.

Results and Discussion

Initial efforts to synthesize metalation–resistant bis(cyclopentadienyl) ligands focused on the bis(ethylene) bridged compound $(C_5H_2\text{–}1\text{–}CMe_3)_2(\mu\text{–}CH_2CH_2)_2{}^{2-}$ (Figure 1).

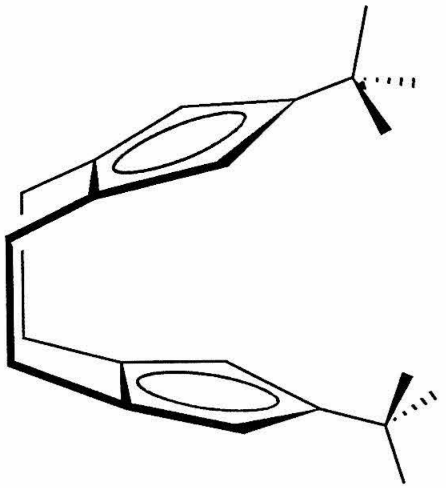
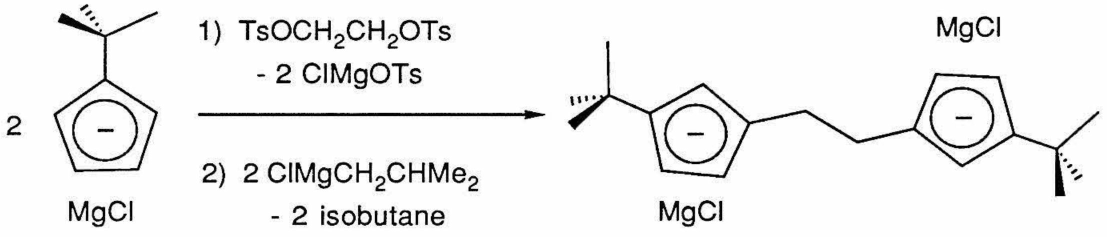


Figure 1

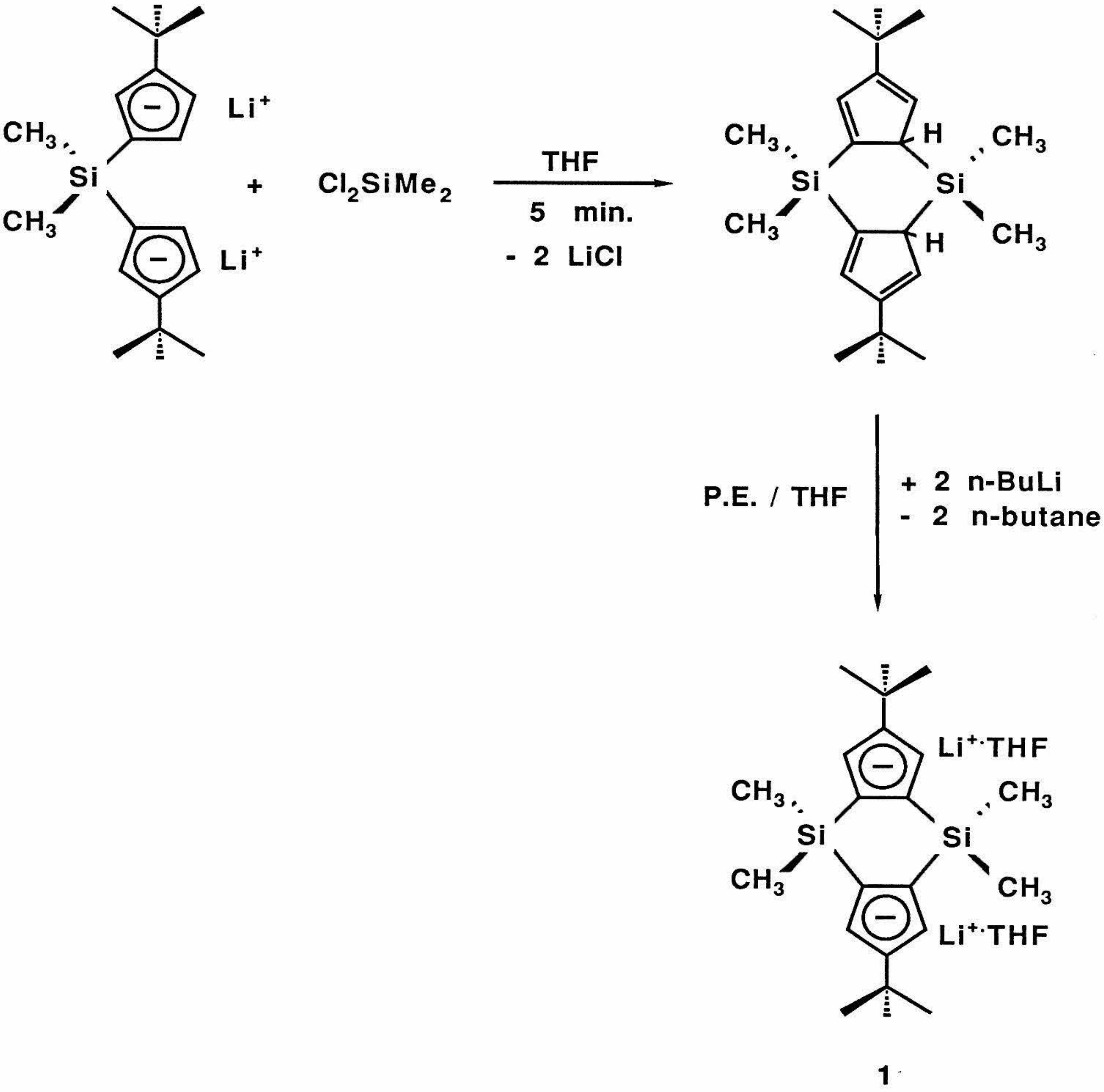
The singly bridged compound $[(C_5H_3\text{–}1\text{–}CMe_3)_2(\mu\text{–}CH_2CH_2)](MgCl)_2$ was prepared in 50% yield by the metathesis reactions depicted in equation 1.[4]



(1)

Despite considerable effort, we were unable to cleanly add a second ethylene bridge to $[(C_5H_3\text{–}1\text{–}CMe_3)_2(\mu\text{–}CH_2CH_2)](MgCl)_2$[5], thus requiring us to pursue an alternative doubly bridged bis(cyclopentadienyl) ligand system.

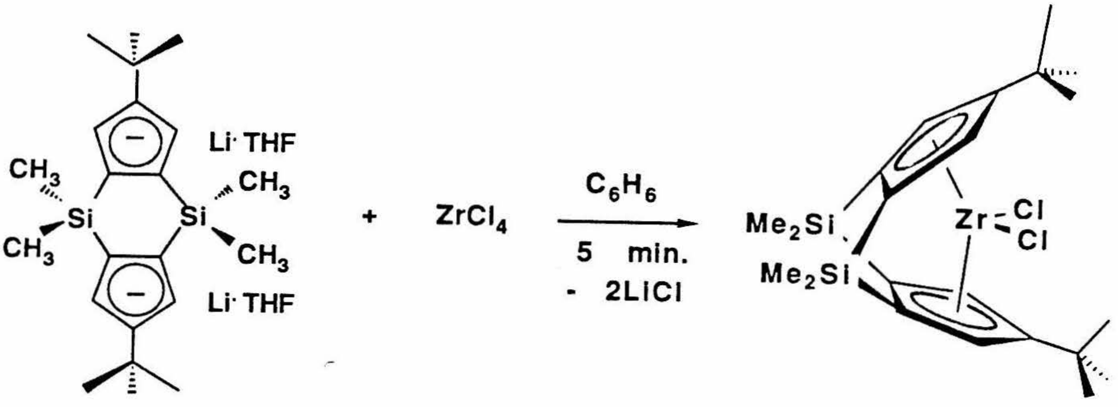
The bis(dimethylsilyl) bridged bis(cyclopentadienyl) ligand $[(\mu\text{–}Me_2Si)_2(C_5H_2\text{–}4\text{–}CMe_3)_2]^{2-}Li^+_2\cdot THF_2$ (1) was prepared from the known mono bridged dianion $(C_5H_3\text{–}3\text{–}{}^tBu)_2(1,1'\text{–}Me_2Si)^{2-}Li^+_2$ (Scheme 1). 1 can be isolated in ca. 50% yield from petroleum ether as a benzene–soluble white powder.



1

Scheme 1. The synthesis of $[(\mu\text{–}Me_2Si)_2(C_5H_2\text{–}4\text{–}CMe_3)_2]^{2-}Li^+_2\cdot THF_2$ (1).

Dianion **1** reacts rapidly (≤ 10 minutes) and quantitatively (^{1}H NMR) with $ZrCl_4$ at room temperature to generate $[(\mu{-}Me_2Si)_2(\eta^5{-}C_5H_2{-}4{-}CMe_3)_2]ZrCl_2$ (**2**) (equation 2).



(2)

1

2

$[(\mu{-}Me_2Si)_2(\eta^5{-}C_5H_2{-}4{-}CMe_3)_2]ZrCl_2$ (**2**) (abbreviated as $BsZrCl_2$[6]) can be isolated in 89% yield from petroleum ether as an off–white powder. In order to confirm the assignment of **2** as a monomeric zirconocene derivative the structure has been determined by X–ray diffration techniques.

A molecular view of $BsZrCl_2$ is presented in Figure 2; another view including the atomic labeling is shown in Figure 3. The most unusual feature of $BsZrCl_2$ is the dihedral angle of 73(4) ° formed by the cyclopentadienyl ring planes. Typical values for dihedral angles of the group IV metallocenes are on the order of 45–50 °.[7] As a consequence of this unusual dihedral angle, the cyclopentadienyl ring carbon to zirconium distances vary widely (Table 2). The shortest distances are from zirconium to the ring carbons bonded to the dimethylsilyl bridges, C11A, C11B, C21A, and C21B ($Zr{-}C_{(avg)} = 2.415(5)$ Å). The largest distances are from zirconium to the carbons bearing the *tert*–butyl substituent, C13 and C23 ($Zr{-}C_{(avg)} = 2.676(5)$ Å). The carbon–carbon distances within the two

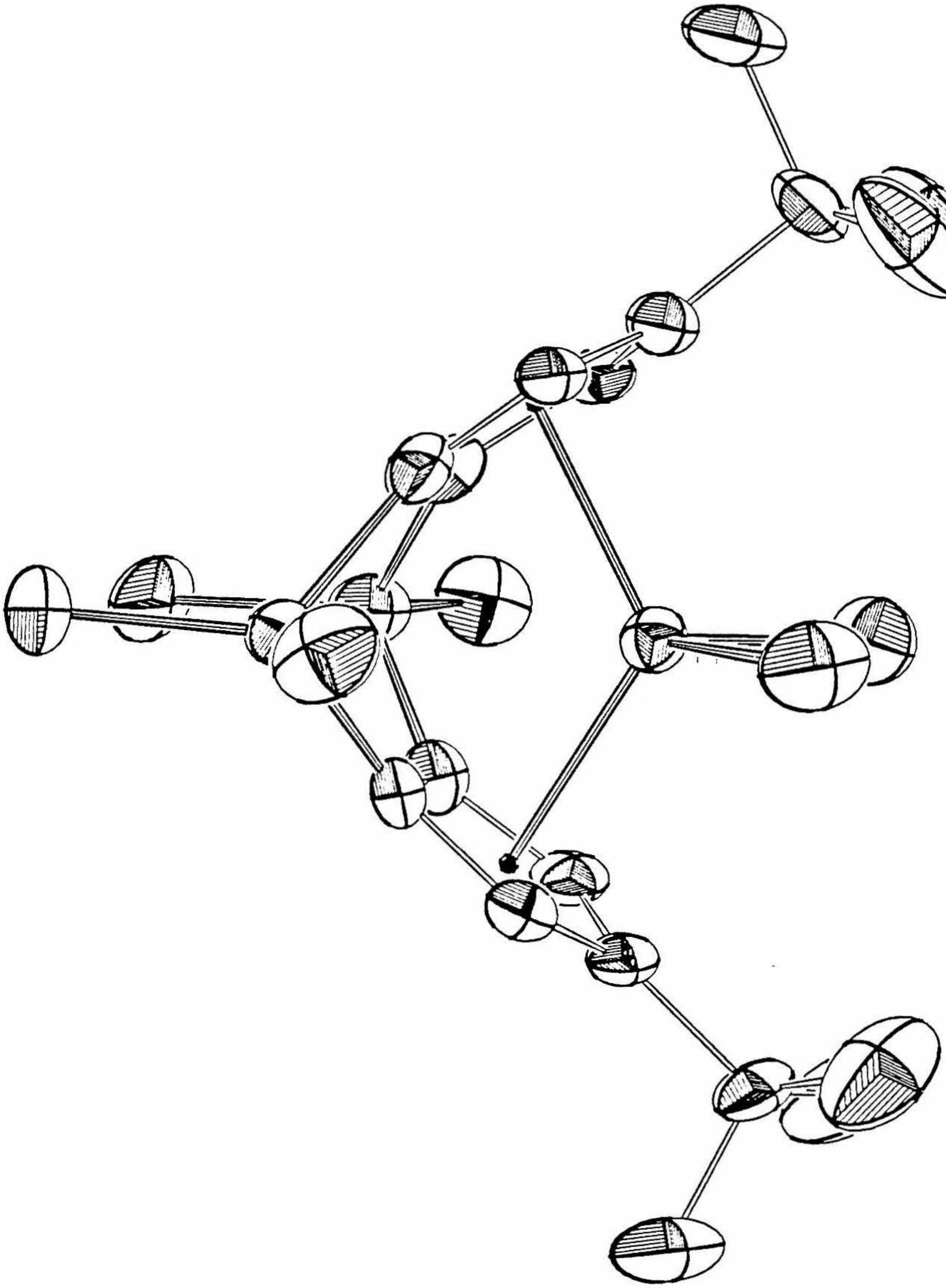


Figure 2. A molecular view of **2**. The thermal ellipsoids are shown at the 50% probability level.

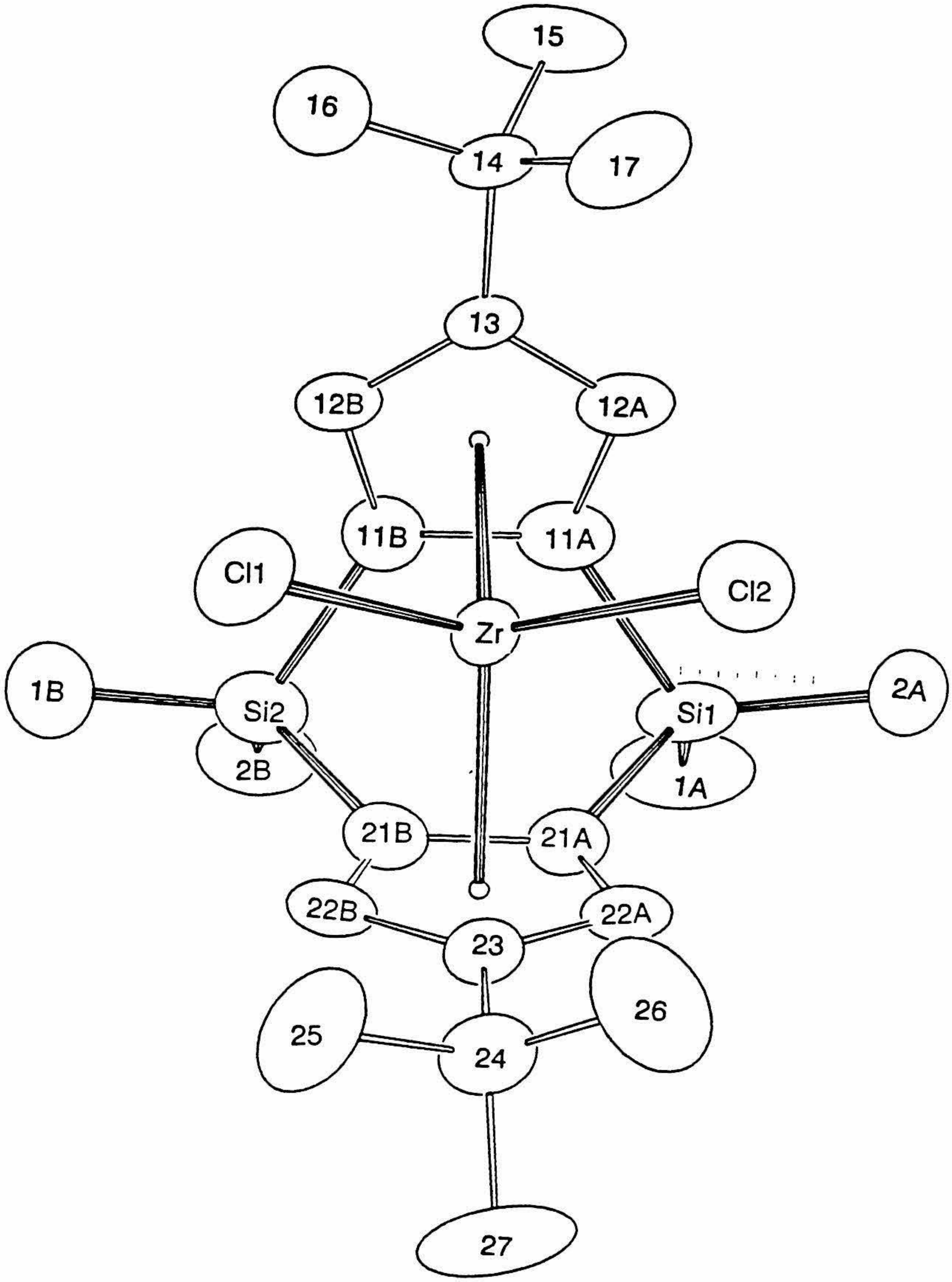


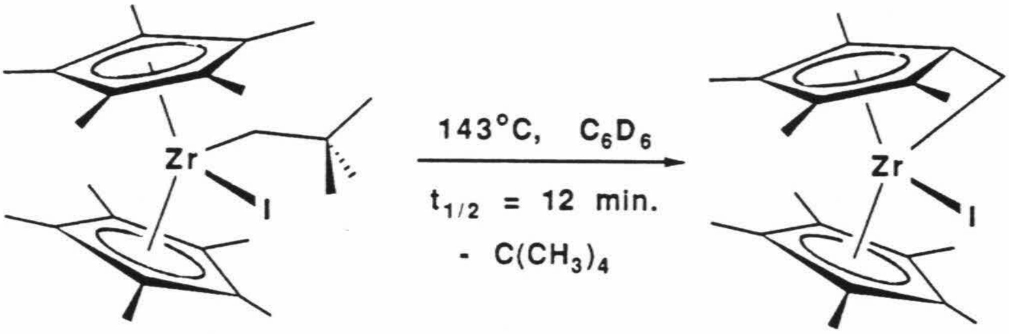
Figure 3. A molecular view of **2** including atomic labels.

Table 2. Selected Distances and Angles for $BsZrCl_2$ (**2**).

Atom	Atom	Dist. (Å)	Atom	Atom	Atom	Angle
Zr	Cl1	2.427(5)	Cl1	Zr	Cl2	101.9(1)
Zr	Cl2	2.419(5)	C11A	Si1	C21A	92.4(2)
Zr	C11A	2.418(5)	C11B	Si2	C21B	92.2(2)
Zr	C11B	2.416(5)	C1A	Si1	C2A	109.2(3)
Zr	C12A	2.570(5)	C2A	Si2	C2B	109.8(3)
Zr	C12B	2.567(5)	C12A	C11A	C11B	105.9(4)
Zr	C13	2.688(5)	C12B	C11B	C11A	105.6(4)
Zr	C21A	2.408(5)	C13	C12A	C11A	110.4(4)
Zr	C21B	2.417(5)	C13	C12B	C11B	111.3(4)
Zr	C22A	2.560(5)	C12B	C13	C12A	106.9(4)
Zr	C22B	2.554(5)	C22A	C21A	C21B	107.1(4)
Zr	C23	2.663(5)	C22B	C21B	C21A	105.9(4)
Si1	C11A	1.870(5)	C23	C22A	C21A	110.5(5)
Si1	C21A	1.889(5)	C23	C22B	C21B	110.7(5)
Si1	C1A	1.872(7)	C22B	C23	C22A	105.8(5)
Si1	C2A	1.870(6)				
Si2	C11B	1.871(5)				
Si2	C21B	1.878(5)				
Si2	C1B	1.853(7)				
Si2	C2B	1.855(7)				
C11A	C11B	1.466(7)				
C11A	C12A	1.427(7)				
C11B	C12B	1.417(7)				
C12A	C13	1.394(7)				
C12B	C13	1.390(7)				
C13	C14	1.512(7)				
C14	C15	1.503(10)				
C14	C16	1.484(10)				
C14	C17	1.516(9)				
C21A	C21B	1.448(7)				
C21A	C22A	1.397(7)				
C21B	C22B	1.408(7)				
C22A	C23	1.407(7)				
C22B	C23	1.408(7)				
C23	C24	1.527(7)				
C24	C25	1.504(8)				
C24	C26	1.511(9)				
C24	C27	1.499(9)				

cyclopentadienyl rings also vary dramatically. The longest carbon–carbon bonds are the C11A–C11B and the C21A–C21B distances of 1.466(7) and 1.448(7) Å, respectively. The remaining carbon–carbon bond distances are substantially shorter, ranging from the C12B to C13 distance of 1.390(7) Å, to the C11A to C12A distance of 1.427(7) Å.

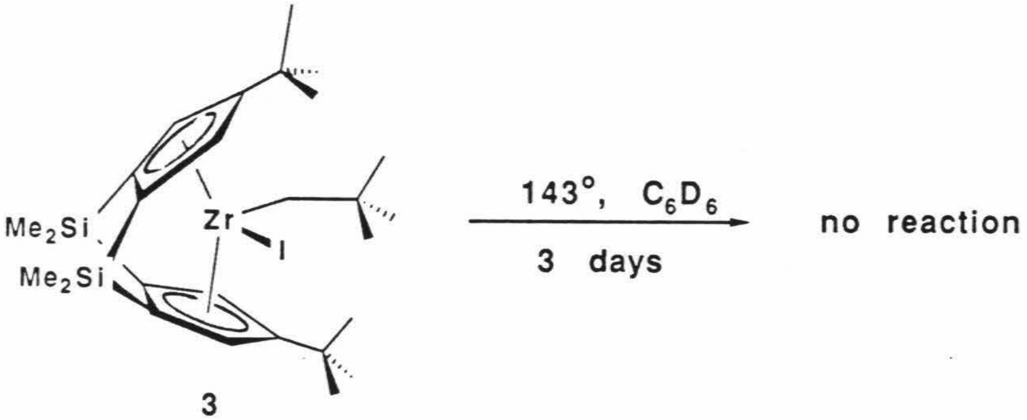
The complexes BsZr(CH_2CMe_3)I (**3**) and Cp*$_2$Zr(CH_2CMe_3)I (**4**) were prepared by established methods[8], thus allowing for the relative stability of a pair of Cp* and Bs ligated zirconium derivatives to be compared. Heating benzene–d_6 solutions of **4** at 143 °C results in the liberation of neopentane and the formation of Cp*(η^5,η^1–$C_5Me_4CH_2$)ZrI (equation 3).



4

(3)

The disappearance of **4**, as monitored by Cp* peak height versus internal Cp_2Fe, follows first order kinetics for 3 half lives with a rate constant of 8.6(5) x 10^{-4} s^{-1} ($t_{1/2}$ = 12.5 minutes at 143 °C). In contrast, heating benzene–d_6 solutions of **3** for three days at 143 °C results in



3

(4)

less than 10% loss of intensity of the *tert*–butyl peak height versus an internal standard (equation 4). Thus, the bis(pentamethylcyclopentadienyl) ligated complex **4** decomposes ≥ 3 x 10^3 times more rapidily at 143°C than does the $[(\mu\text{–Me}_2\text{Si})_2(\eta^5\text{–C}_5\text{H}_2\text{–4–CMe}_3)_2]$ ligated complex **3**.

In summary, a synthetically useful route to the doubly bridged bis(cyclopentadienyl) ligand $[(\mu\text{–Me}_2\text{Si})_2)(\text{C}_5\text{H}_2\text{–4–CMe}_3)_2]^{2-}\text{Li}^+{}_2\bullet\text{THF}_2$ has been developed. This ligand has been used to prepare a series of zirconocene complexes, including the dichloride $[(\mu\text{–Me}_2\text{Si})_2(\eta^5\text{–C}_5\text{H}_2\text{–4–CMe}_3)_2]\text{ZrCl}_2$ (**2**) which has been crystallographically characterized. The presence of two adjacent dimethylsilyl bridges results in an unusually large dihedral angle formed by the cyclopentadienyl rings of **2**. A comparison of the thermal stabilities (at 143°C) of the complexes $[(\mu\text{–Me}_2\text{Si})_2(\eta^5\text{–C}_5\text{H}_2\text{–4–CMe}_3)_2]\text{Zr}(\text{CH}_2\text{CMe}_3)\text{I}$ (**3**) and $(\eta^5\text{–C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2\text{CMe}_3)\text{I}$ (**4**) reveals that the former is ≥ 3 x 10^3 times more stable than the latter. While these results should be considered preliminary, they do suggest that early transition metal complexes of Bs can be prepared and show increased thermal stabilty as compared to their pentamethylcyclopentadienyl analogs. Efforts are presently underway to extend the range of Bs–ligated complexes to more electropositive metals such as scandium.

Table 1. ^{1}H and ^{13}C NMR data.^{a}

Compound	Assignment	δ (ppm)	Coupling^b
$[(\mu\text{–}\mathrm{Me_2Si})_2(\mathrm{C_5H_2\text{–}4\text{–}CMe_3})_2]^{2-}\mathrm{Li^+}_2\cdot\mathrm{THF_2}$ (1)			
	$\mathrm{C(C}\mathit{H}_3)_3$	1.52 s	
	$\mathrm{Si(C}\mathit{H}_3)_2$	0.68 s	
	$\mathrm{C_5}\mathit{H}_2$	6.63 s	
	THF(β)	0.95 m	
	THF(α)	2.92 m	
$[(\mu\text{–}\mathrm{Me_2Si})_2(\eta^5\text{–}\mathrm{C_5H_2\text{–}4\text{–}CMe_3})_2]\mathrm{ZrCl_2}$ (2)			
	$\mathrm{C(C}\mathit{H}_3)_3$	1.44 s	
	$\mathrm{Si(C}\mathit{H}_3)_2$	0.32 s	
		0.57 s	
	$\mathrm{C_5}\mathit{H}_2$	6.83 s	
	$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	32.14 q	$^1J_{CH}$ = 125
	$\mathit{C}\mathrm{(CH_3)_3}$	32.98 s	
	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$	–3.94 q	$^1J_{CH}$ = 122
		4.23 q	$^1J_{CH}$ = 123
	Cp–C_1,C_2	113.8 s	
	Cp–C_3,C_5	136.7 d	$^1J_{CH}$ = 169
	Cp–C_4	143.4 s	
$[(\mu\text{–}\mathrm{Me_2Si})_2(\eta^5\text{–}\mathrm{C_5H_2\text{–}4\text{–}CMe_3})_2]\mathrm{ZrI_2}$			
	$\mathrm{C(C}\mathit{H}_3)_3$	1.60 s	
	$\mathrm{Si(C}\mathit{H}_3)_2$	0.30 s	
		0.47 s	
	$\mathrm{C_5}\mathit{H}_2$	7.12 s	
$[(\mu\text{–}\mathrm{Me_2Si})_2(\eta^5\text{–}\mathrm{C_5H_2\text{–}4\text{–}CMe_3})_2]\mathrm{Zr(CH_2CMe_3)I}$ (3)			
	$\mathrm{C(C}\mathit{H}_3)_3$	1.47 s	
	$\mathrm{Si(C}\mathit{H}_3)_2$	0.23 s	
		0.45 s	
		0.48 s	
		0.50 s	
	$\mathrm{C_5}\mathit{H}_2$	7.13 s	
		7.16 s	
	$\mathrm{CH_2C(C}\mathit{H}_3)_3$	1.12 s	
	$\mathrm{C}\mathit{H}_2\mathrm{CMe_3}$	0.77 s	

$Cp^*_2Zr(CH_2CMe_3)I$ (4)

$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_5}$	1.85 s	
$\mathrm{CH_2C(C}\mathit{H}\mathrm{_3)_3}$	1.22 s	
$\mathrm{C}\mathit{H}\mathrm{_2C(CH_3)_3}$	0.90 s	

$Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)ZrI$

$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_5}$	1.88 s	
$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_4CH_2}$	1.33 s	
	1.57 s	
	1.95 s	
	2.18 s	
$\mathrm{C_5(CH_3)_4C}\mathit{H}\mathrm{_2}$	1.45 d	$^2J_{HH} = 7.5$
	not observed	

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[a] All NMR spectra were recorded in benzene–d_6 and are referenced to internal tetramethylsilane.
[b] Coupling constants are reported in hertz.

Note: The following abbreviations are used to denote the multiplicity of the NMR signals: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Experimental Section

General Considerations. All manipulations were performed using glovebox, high–vacuum[9] or Schlenk techniques. Solvents were purified by distillation from an appropriate drying agent under a N_2 atmosphere and either used immediately or vacuum–transferred from "titanocene" or sodium–benzophenone. Benzene–d_6 was purified by vacuum transfer from activated molecular sieves (4 Å, Linde) and then from "titanocene". ^1H and ^{13}C NMR spectra were measured on Varian EM–390 (90 MHz) and JEOL GX400Q (400 MHz, ^1H; 100 MHz, ^{13}C)) spectrometers. Elemental analyses were performed by Mr. L. Henling of the CIT Analytical Laboratory.

Synthetic Procedures

$[(\mu\text{–}Me_2Si)_2(C_5H_2\text{–}4\text{–}CMe_3)_2]^{2-}Li^+_2\cdot THF_2$ (1). Under an argon atmosphere, Me_2SiCl_2 (4.3 mLs, 34 mmol) was slowly syringed into a well stirred tetrahydrafuran solution of $[(C_5H_3\text{–}3\text{–}CMe_3)_2(\mu\text{–}Me_2Si)]^{2-}Li^+_2$[10] (10.7 g, 34 mmol). The resulting suspension was stirred for one hour, after which the majority of the tetrahydrafuran was removed *in vacuo*. Approximately 90 mL of petroleum ether was condensed into the flask and the suspension was filtered to remove the LiCl. 2.2 equivalents of *n*–butyllithium (47 mL of a 1.6 M hexane solution) was slowly syringed into the resulting solution. After *ca*. 20 minutes a white precipitate formed which was isolated by filtration. Yield: 10.0 g (57%).

$[(\mu\text{–}Me_2Si)_2(C_5H_2\text{–}4\text{–}CMe_3)_2]ZrCl_2$ (2). Approximately 50 mL of benzene was condensed onto a mixture of 1 (10.0 g, 19.5 mmol) and $ZrCl_4$ (5.0 g, 21.4 mmol). After stirring this mixture for 2 hours the suspension was filtered to remove LiCl and the benzene was removed *in vacuo.* Approximately 80 mL of petroleum ether was condensed onto the product. Filtering this suspension yielded 8.8 g (2 crops) of product as an off–white powder (89% yield). The dichloride is often contaminated with traces of THF.

[(μ–Me$_2$Si)$_2$(C$_5$H$_2$–4–CMe$_3$)$_2$]ZrI$_2$. Approximately 50 mL of benzene was condensed onto a mixture of **2** (3.7 g, 7.3 mmol) and excess BI$_3$ (2.8 g, 7.2 mmol). After stirring for 1 hour the benzene was replaced with diethyl ether. Filtering the resulting suspension afforded 3.24 g of the yellow product (64%).

[(μ–Me$_2$Si)$_2$(C$_5$H$_2$–4–CMe$_3$)$_2$]Zr(CH$_2$CMe$_3$)I (4). Approximately 25 mLs of benzene was condensed onto a mixture of [(μ–Me$_2$Si)$_2$(C$_5$H$_2$–4–CMe$_3$)$_2$]ZrI$_2$ (1.6 g, 2.29 mmol) and LiCH$_2$CMe$_3$ (215 mg, 2.75 mmol). After stirring for 1 hour the suspension was filtered and the benzene was replaced with petroleum ether. Cooling to –78 °C and filtering afforded 0.91 g (62%) of bright yellow product. Elemental analysis: Found(calculated) %C 49.78 (50.36), %H 6.69 (7.04).

Kinetics of the decomposition of Cp*$_2$Zr(CH$_2$CMe$_3$)I (4) and BsZr(CH$_2$CMe$_3$)I (3). Approximately 30 mg of **4** was sealed in a NMR tube with *ca.* 5 mg of FeCp$_2$ and *ca.* 0.5 mL of benzene–d_6. The reaction were followed by monitoring the decrease in intensity of the *tert*–butyl resonance of **4** at δ 1.22 relative to internal Cp$_2$Fe. NMR spectra were recorded at timed intervals using a Varian EM–390 (90 MHz) spectrometer. Peak heights were demonstrated to be reproducible to within ± 7% by repeated measurement. Each spectrum was recorded 3 times and the averaged peak height was used to calculate the rate constant. The reaction temperature of 143 °C was maintained using a constant temperature oil bath controlled by thermoregulators and was observed to be constant to within ± 1°C. The thermolysis of BsZr(CH$_2$CMe$_3$)I (**3**) was followed by monitoring the decrease in the *tert*–resonance at δ 1.47. In order to assure an unreactive internal standard, hexamethylbenzene in benzene–d_6 was sealed in a melting point capillary which was subsequently added to the NMR tube used for kinetic measurements.

References:

(1) (a) Chapters I and II of this thesis. (b) McDade, C., Green, J. C., Bercaw, J. E. *Organometallics*, **1982**, *1*, 1629. (c) Pattiasina, J. W., Hissink, C. E., de Boer, J. L., Meetsma, A., Teuban, J. H., and Spek, A. L., *J. Am. Chem. Soc.*, **1985**, *107*, 7758-7759. (d) Parkin, G. F. B. C. and Bercaw, J. E. *unpublished results*.

(2) Thompson, M. E., Baxter, S. M., Bulls, A. R. Burger, B. J., Nolan, M. C., Santarsiero, B. D., Schaefer, W. P., Bercaw, J. E. *J. Am. Chem. Soc.*, **1987**, *109,* 203.

(3) Lauher, J. W., Hoffmann, R. *J. Am. Chem. Soc.*, **1976**., *98,* 1729–1742.

(4) While the yield of the mono bridged dianion $[(C_5H_3{-}1{-}CMe_3)_2(\mu{-}CH_2CH_2)(MgCl)_2$ is *ca.* 50%, its purity is only *ca.* 85% (^{1}H NMR), which undoubtedly contributes to the lack of success in adding a second ethylene bridge.

(5) The reaction of $[(C_5H_3{-}1{-}CMe_3)_2(\mu{-}CH_2CH_2)(MgCl)_2$ with one equivalent of $TsOCH_2CH_2OTs$, followed by deprotonation with *n*–butyllithium yields an intractable mixture. Adding $ScCl_3 \cdot THF_3$ to suspensions of this crude mixture, followed by sublimation at 130 °C, does afford $(\eta^5{-}C_5H_2{-}1{-}CMe_3)_2(\mu{-}CH_2CH_2)_2ScCl \cdot THF$ in *ca.* 1% yield.

(6) The abbreviation Bs is derived from bis(dimethylsilyl) bridged bis(cyclopentadienyl).

(7) See for example: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*; Academic Press: New York, N.Y. **1974**, and references therein.

(8) $Cp^*_2Zr(CH_2CMe_3)I$ was prepared as described for its hafnium analogue in Chapter 1.

(9) Burger, B. J.; Bercaw, J. E. in "New Developments in the Synthesis, Manipulation and Characterization of Organometallic Compounds", *ACS Symposium Series,* A. Wayda and M. Darensbourg, Eds., in press.

(10) Bunel, E.; Bercaw, J. E. *Organometallics*, Manuscript in preparation

Chapter 4

Relative Bond Dissociation Energies for Early Transition Metal Alkyl, Aryl, Alkynyl and Hydride Compounds. Equilibration of Metallated Cyclopentadienyl Derivatives of Peralkylated Hafnocene and Scandocene Derivatives with Hydrocarbons and Dihydrogen.

Abstract: Relative bond dissociation energies (BDEs) have been obtained by equilibrating early transition metal alkyls and hydrides with H_2 or the C–H bonds of hydrocarbons. Thus, in benzene solution $Cp^*_2HfH_2$ ($Cp^* = (\eta^5\text{–}C_5Me_5)$) equilibrates with $Cp^*_2Hf(C_6H_5)H$ and dihydrogen. From the enthalpy of the reaction, $\Delta H^\circ = +6.0(3)$, the Hf–H (BDE) is calculated to be 0.8(3) $kcal{\cdot}mol^{-1}$ stronger than the $Hf\text{–}C_6H_5$ BDE. Relative $Sc\text{–}C_6H_5$ and Sc–alkyl BDEs have been estimated from the equilibration of the metallated complex $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)Sc$, C_6H_6 and $Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)Sc(C_6H_5)$, the $Sc\text{–}C_6H_5$ BDE being 16.6(3) $kcal{\cdot}mol^{-1}$ stronger than the $Sc\text{–}CH_2CH_2CH_2C_5Me_4$ BDE. From a similar reversible intramolecular metallation of $Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)HfH_2$ to give $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)HfH$ and dihydrogen, the Hf–H BDE is estimated to be 23.0(3) $kcal{\cdot}mol^{-1}$ stronger than the $Hf\text{–}CH_2CH_2CH_2C_5Me_4$ BDE. The equilibration of $Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)Sc\text{–}C{\equiv}CCMe_3$ with the metallated scandocene derivative $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_4)Sc$ and *tert*–butylacetylene lies very far towards $Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)Sc\text{–}C{\equiv}CCMe_3$, so that only a lower limit for the relative Sc–alkynyl and Sc–aryl BDEs may be determined: BDE(Sc–alkynyl) – BDE(Sc–aryl) $\geq$ 29(5) $kcal{\cdot}mol^{-1}$. These early transition metal–hydrocarbyl (M–R) BDEs correlate with the corresponding H–R BDEs (*i.e.* M–alkynyl > M–aryl > M–alkyl); however, the M–R BDEs increase more rapidly with s character than does the H–R BDEs. The origin of this effect is not known, but it is undoubtedly also responsible for the characteristically high M–H BDEs for transition metal hydride compounds. In an effort to probe the polarity of Sc–aryl bonds a series of scandocene derivatives capable of reversibly metallating at either of two differently substituted benzyl groups was prepared. The equilibrium constants for these metallated derivatives: $(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_3\text{–}p\text{–}X)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)Sc \rightleftharpoons (\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}X)(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_3\text{–}p\text{–}CH_3)Sc$ ($X = H, CF_3, NMe_2$) were determined. The small dependence of K_{eq} on the nature of X suggests that the Sc–aryl bond is essentially covalent with only a slight ionic character.

Introduction

Early transition metals form many stable compounds with electronegative ligands such as halogens due to the high degree of ionic character of the M–X bond. Strong bonds between early transition metals and oxygen- or nitrogen-containing ligands (*e.g.* OR, NR_2) have this same feature. Moreover, multiple M=X or M≡X bonding may also obtain by donation of one or two electron pairs from X to empty orbitals on the metal. The later, less electropositive transition metals also form strong bonds to these heteroatoms[1]; however, early metal–heteroatom bonds are generally more robust. The strength of early transition metal-carbon and early transition metal-hydrogen bonds relative to the strengths of those of the middle and late transition metals is somewhat less straightforward to predict. *A priori*, we might expect that they would also be systematically greater since the bond homolysis ($L_mM^n–R \longrightarrow L_mM^{n-1} + \cdot R$) formally involves reducing the metal by one unit. Electropositive metals have higher reduction potentials (for a given oxidation state) as compared with the more electronegative transition metals to the right. Furthermore, a comparison of the electronegativities of carbon, hydrogen, and the various transition metals reveals that some ionic character ($M^{\delta+}–R^{\delta-}$; R = H, C) may be expected when M is an early transition metal. Indeed, the reactions of early metal hydrides and alkyls with protic reagents such as mineral acids and water, which rapidly evolve H_2 and RH, suggest just such polarization.[2] Little direct experimental evidence is available which is indicative of the amount of ionic character for early transition metal-carbon or -hydrogen bonds, however. Moreover, Mulliken populations obtained from quantum mechanical calculations are generally unreliable indicators of the ionic character of M–R bonds.[3] Likewise, little experiment evidence is available which reflects the dependence of the M–R BDE on the hybridization at the α

carbon, *i.e.* the quantitative differences in the series: metal–alkyl *vs.* metal–alkenyl *vs.* metal–aryl *vs.* metal–alkynyl.

In this chapter are described some experiments designed to address these issues. Although we have thus far been unable to obtain reliable absolute bond dissociation energies (BDEs), we have been able to derive accurate relative BDEs by equilibrating early transition metal alkyls and hydrides with the C–H bonds of hydrocarbons *via* the rapid, reversible "sigma bond metathesis" reactions[4] characteristic of early transition metals, lanthanides and actinides (equation 1).

$$L_nM{-}R + R'{-}H \rightleftharpoons L_nM{-}R' + R{-}H \qquad (1)$$

(R, R' = H, alkyl, alkenyl, aryl, alkynyl)

Reported for peralkylated-scandocene and -hafnocene derivatives are (*i*) relative M–H and M–C BDEs (M = Sc, Hf), (*ii*) relative bond strengths of scandium- and hafnium-carbon bonds as the hybridization at carbon is varied, and (*iii*) relative Sc–aryl BDEs as the aryl substitutent is systematically varied.

Results

Determination of Relative M-H and M-Ph Bond Dissociation Energies via Intermolecular Equilibration. As previously reported[7], the clean, reversible nature of the reaction of *bis*(pentamethylcyclopentadienyl)scandium hydride, $Cp^*_2Sc{-}H$ (Cp^* = ($\eta^5{-}C_5Me_5$)) with benzene (equation 2) permits a determination of the relative Sc–H and $Sc{-}C_6H_5$ BDEs: the Sc–H BDE is 1.5 kcal mol^{-1} greater than the $Sc{-}C_6H_5$ BDE.

$$Cp^*_2Sc{-}C_6H_5 + H_2 \rightleftharpoons Cp^*_2Sc{-}H + H{-}C_6H_5 \qquad (2)$$

In a similar manner $Cp^*_2HfH_2$ in benzene solution at ≥ 100 °C cleanly establishes an equilibrium with $Cp^*_2Hf(H)(C_6H_5)$ and dihydrogen (equation 3).

$$Cp^*_2HfH_2 + H\text{–}C_6H_5 \rightleftharpoons Cp^*_2Hf(H)(C_6H_5) + H_2 \tag{3}$$

$Cp^*_2Hf(C_6H_5)_2$ is not observed under these conditions. The enthalpy and entropy of equilibrium 3, $\Delta H^\circ = +6.0(3)\ \mathrm{kcal \cdot mol^{-1}}$ and $\Delta S^\circ = +3.5(5)$ e.u., are obtained from the temperature dependence of the equilibrium (Table 1, Figure 1).

Table 1. Equilibrium constants for the equilibrium between $Cp^*_2Hf(C_6H_5)H$ and $Cp^*_2HfH_2$ in C_6H_6 (equation 3).

Temperature (°C)	K_{eq} (x 10^5)
100.5	5.27
109	5.91
129	8.57
144	12.1
171	18.6

$\Delta H^\circ = + 6.0(3)\ \mathrm{kcal \cdot mol^{-1}}$

$\Delta S^\circ = + 3.5(5)$ e.u.

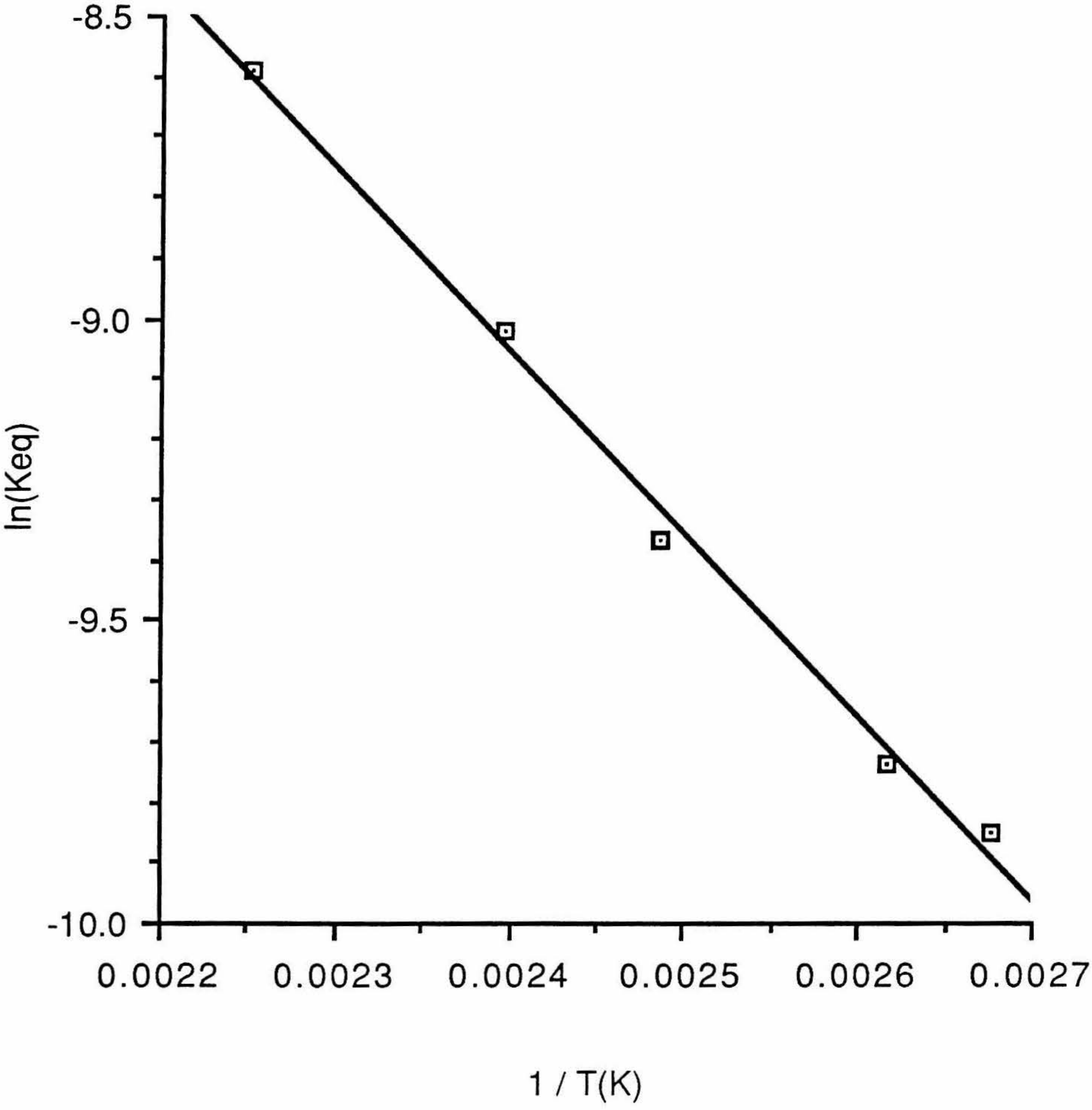


Figure 1. van't Hoff plot for the equilibrium between $Cp^*_2Hf(C_6H_5)H$ and $Cp^*_2HfH_2$ in C_6H_6.

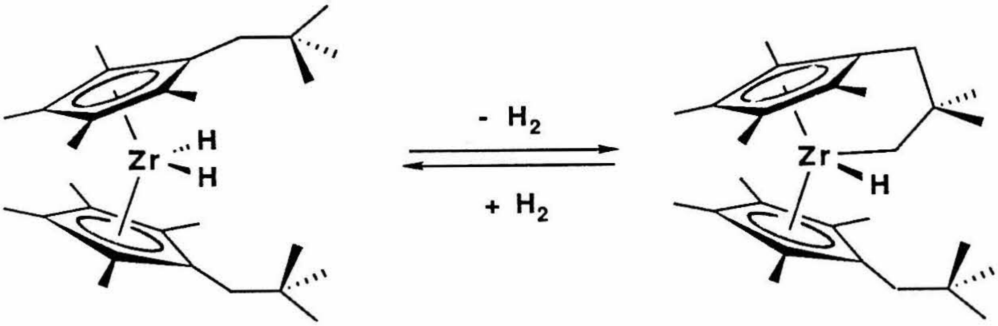
Attempts to extend this approach to include equilibration of alkanes with permethylhafnocene or permethylscanodcene hydrides or alkyls were unsuccessful, possibly due to interfering reactions of the C–H bonds of the pentamethylcyclopentadienyl ligands.[7] For example, thermolyzing $Cp^*_2Sc{-}C_6H_5$ with mesitylene, tetramethylsilane, or n–butane, either neat or with varying concentrations of benzene, results in the slow decomposition to a mixture of uncharacterized scandium–containing products. The expected reaction products, $Cp^*_2Sc{-}R$ ($R = CH_2C_6H_3{-}3{,}5{-}(CH_3)_2$, CH_2SiMe_3, $CH_2CH_2CH_2CH_3$), have been independently synthesized, and each reacts with benzene to generate $Cp^*_2Sc{-}C_6H_5$ and $H{-}R$ (equation 4).

$$Cp^*_2Sc{-}R \;+\; C_6H_6 \;\rightleftharpoons\; Cp^*_2Sc{-}C_6H_5 \;+\; H{-}R \qquad (4)$$

$R = CH_2C_6H_3{-}3{,}5{-}(CH_3)_2$
$= CH_2SiMe_3$
$= CH_2CH_2CH_2CH_3$

Thus, the reactions of $Cp^*_2Sc{-}C_6H_5$ with these reagents appear to be so thermodynamically unfavorable as to prevent buildup of detectable concentrations of permethylscandocene derivatives other than $Cp^*_2Sc{-}C_6H_5$.

Determination of Relative M-H and M-C Bond Dissociation Energies via Intramolecular Equilibration. We have previously shown that *bis*(tetramethylneopentylcyclopentadienyl)zirconium dihydride is in facile equilibrium with the metallated mono–hydride complex and dihydrogen (equation 5).[5]



(5)

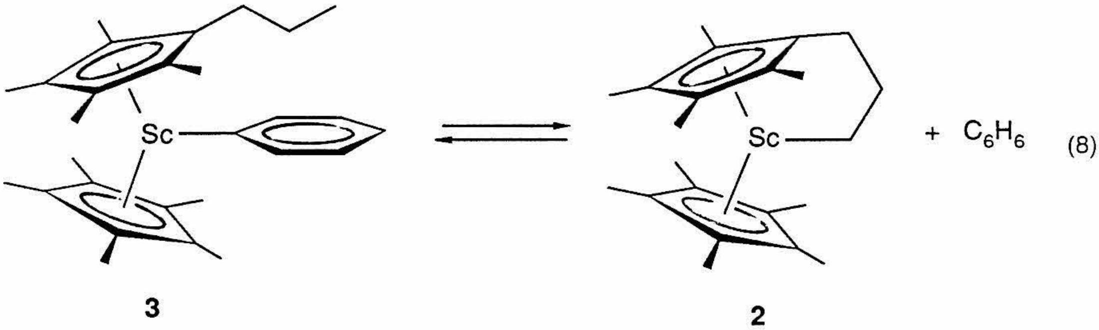
With the hope that these types of equilibria are quite general, we have undertaken the syntheses of compounds which would allow intramolecular equilibration *via* sigma bond metathesis reactions of Sc–R with the C–H bonds of appended alkyl, aryl, *etc.* groups. Thus, the mixed-Cp scandocene chloride **1** has been prepared as shown in equation 6. Heating $(Cp^*ScCl_2)_n$ with one equivalent of $Li^+(C_5Me_4CH_2CH_2CH_3)^-$ yields complex **1** as an amber oil (> 90% pure by ^1H NMR).

$$(Cp^*ScCl_2)_n \; + \; Li^+(C_5Me_4CH_2CH_2CH_3)^- \xrightarrow[-\,LiCl]{110^oC} \underset{\mathbf{1}}{Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)ScCl} \quad (6)$$

Treatment of **1** with CH_3Li yields $Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)ScCH_3$, which rapidly eliminates methane (< 5 min. at 25°C) to afford $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)Sc$ (**2**) (equation 7).

$$\begin{tikzcd}
Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)ScCl \arrow[r, "+\,CH_3Li,\,-\,LiCl"] & {[Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)ScCH_3]} \arrow[d, "-\,CH_4"] \\
 & \underset{\mathbf{2}}{Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)Sc}
\end{tikzcd} \quad (7)$$

In contrast to other permethylscandocene alkyls, cyclohexane–d_{12} solutions of **2** are quite stable at 140°C. If however, solutions of **2** in cyclohexane–d_{12} are heated with 5–10 equivalents of benzene, an equilibrium consisting of **2**, C_6H_6, and a new species identified as Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)ScC_6H_5 (**3**) is established (equation 8; $\Delta H^o = +3.5(3)$ kcal mol^{-1} and $\Delta S^o = 10.5(5)$ e.u.).



(8)

Table 2. Equilibrium constants for the equilibrium between Cp*(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)Sc and Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)ScC_6H_5 in C_6H_6 (equation 8).

Temperature (°C)	K_{eq}
50	0.65
60	0.78
75	0.96
89.5	1.23
100.5	1.38

$\Delta H° = + 3.5(3)$ kcal · mol^{-1}

$\Delta S° = + 10.5(5)$ e.u.

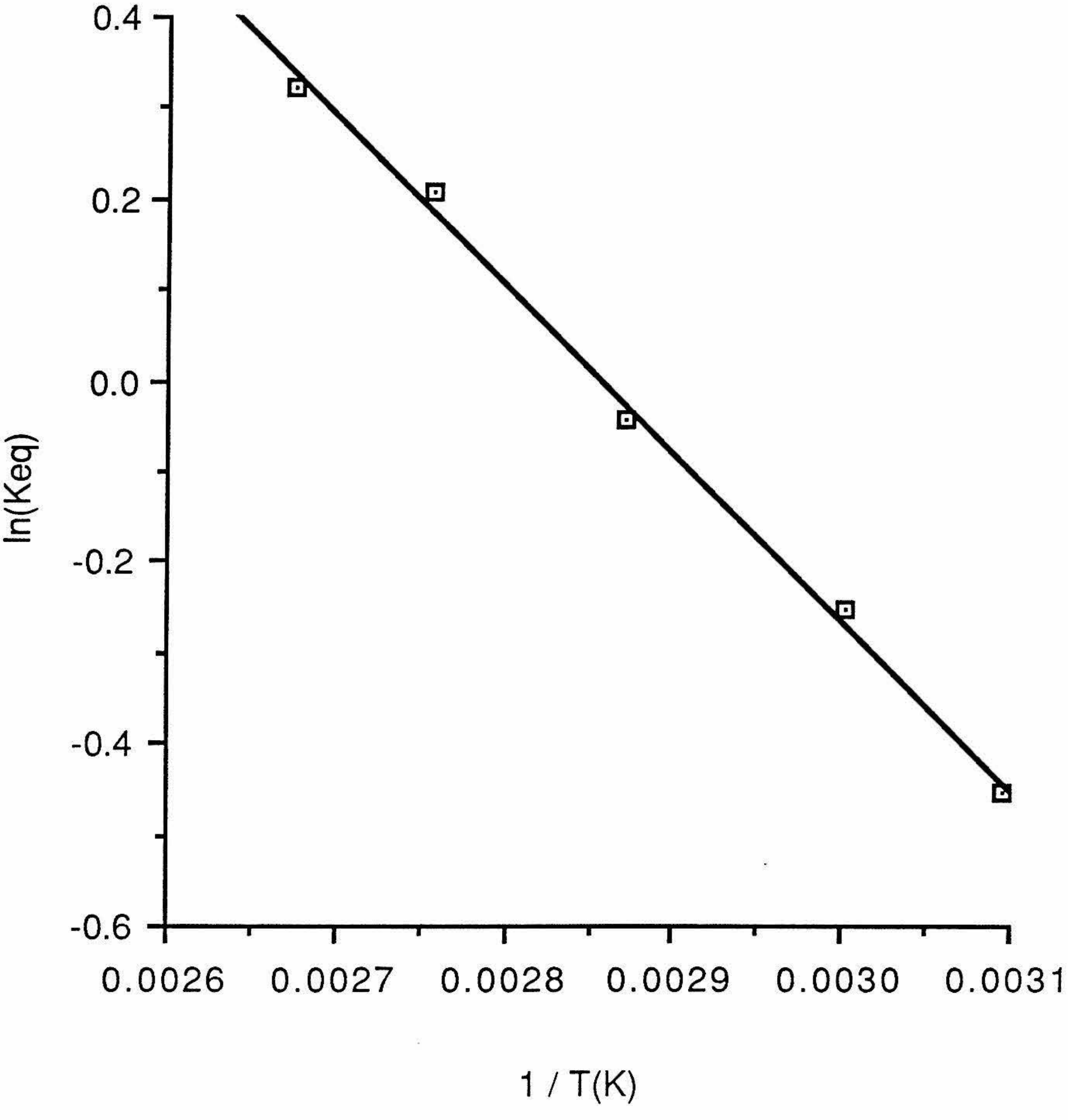
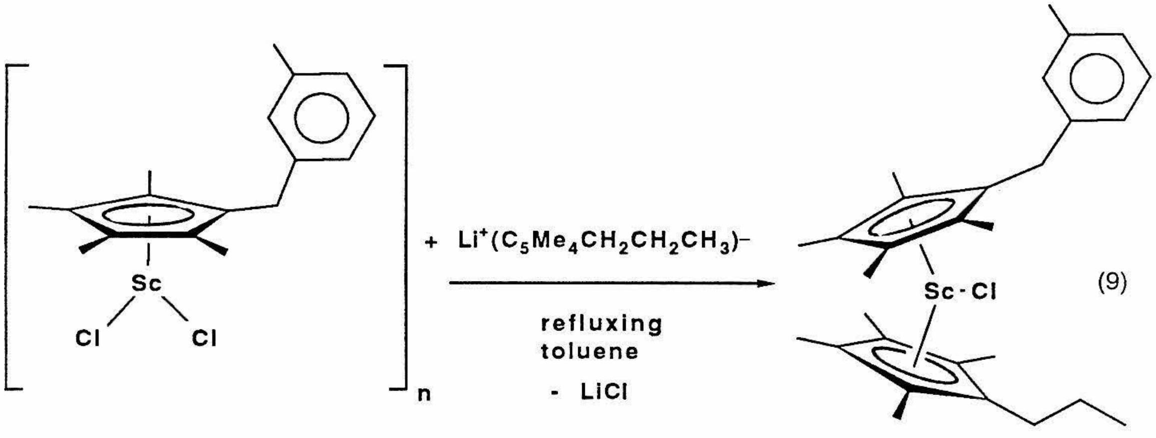


Figure 2. van't Hoff plot for the equilibrium between Cp*(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)Sc and Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)ScC_6H_5 in C_6H_6 (equation 8).

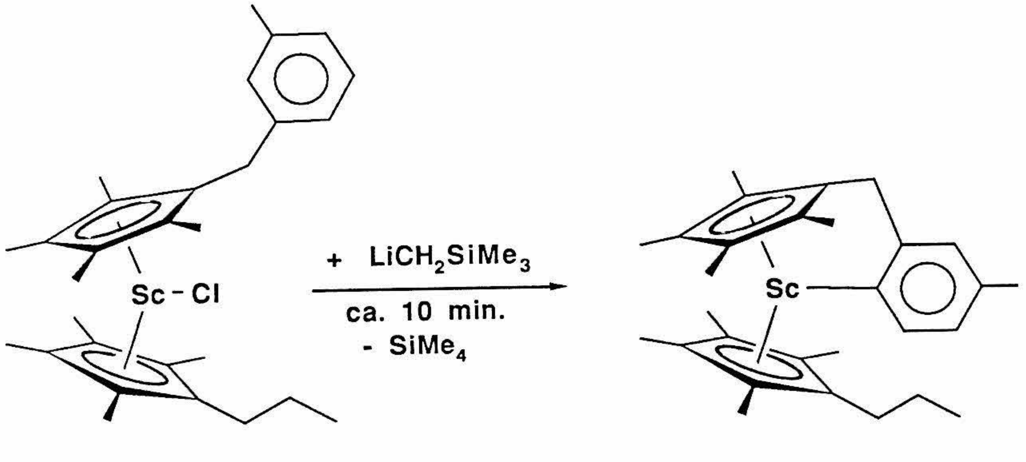
A purely intramolecular equilibration between a pendant alkyl group and a pendant aryl group can be established starting from the mixed–Cp scandocene chloride **4** (equation 9). Treating **4** with one equivalent of trimethylsilylmethyllithium quickly



(9)

4

generates tetramethylsilane and one major product identified as $(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_3\text{–}p\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)Sc$ (**5**) (equation 10).[6]



(10)

4 **5**

Heating benzene–d_6 solutions of **5** for 12 hours does not effect the ^{1}H NMR spectrum. Adding small amounts of dihydrogen to the NMR tube containing benzene–d_6 solutions of 5 results in H/D exchange of the propyl methyl hydrogens of **5** upon thermolysis, but does not otherwise affect the ^{1}H NMR spectrum. An equilibrium is therefore inferred between **5** and (η^5–$C_5Me_4CH_2C_6H_3$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)Sc which is catalyzed by (η^5–$C_5Me_4CH_2C_6H_3$–*m*–CH_3)(η^5–$C_5Me_4CH_2CH_2CH_3$)Sc–H.

That dihydrogen does indeed interconvert **5** and (η^5–$C_5Me_4CH_2C_6H_3$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)Sc is supported by the following observations: (*i*) treating Cp*(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_4)Sc with dihydrogen (4 atm) rapidly yields Cp*(η^5–$C_5Me_4CH_2C_6H_5$)Sc–H, (*ii*) heating benzene–d_6 solutions of Cp*(η^5–$C_5Me_4CH_2C_6H_5$)Sc–H under 4 atmospheres of H_2 results in H/D exchange, specifically into the *ortho* benzylic sites. Based on previous results for H/D exchange between benzene–d_6 and hydrocarbons catalyzed by Cp^*_2Sc–H[4], the likely mechanism for benzylic H/D exchange involves Cp*(η^5–$C_5Me_4CH_2C_6H_5$)Sc–H, Cp*(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_4)Sc, and Cp*(η^5–$C_5Me_4CH_2C_6H_5$)Sc–C_6D_5 (along with H_2, HD, D_2, and $C_6H_nD_{6-n}$).

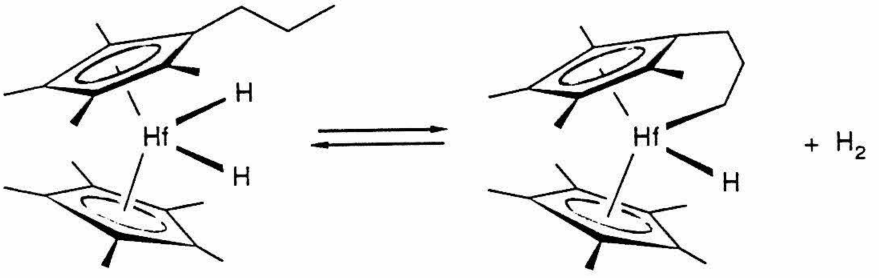
Relative Hf–H and Hf–alkyl BDEs can also be obtained. The mixed-Cp hafnocene complex Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)$HfCl_2$ (**6**) is prepared in high yield from Cp*$HfCl_3$ and $Li^+(C_5Me_4CH_2CH_2CH_3)^-$ (equation 11).

$$\mathrm{Cp^*HfCl_3 + Li^+(C_5Me_4CH_2CH_2CH_3)^-} \xrightarrow[-\ \mathrm{LiCl}]{\text{refluxing xylenes}} \underset{\mathbf{6}}{\mathrm{Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)HfCl_2}} \qquad (11)$$

Treating **6** with n–butyllithium under a dihydrogen atmosphere affords the dihydrido species **5** (equation 12).

$$\underset{\mathbf{6}}{\mathrm{Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)HfCl_2}} \xrightarrow[\substack{2.2\ \text{n–butylLi}\\ -\ 2\ \text{butane}\\ -\ \text{LiCl}}]{\mathrm{H_2}} \underset{\mathbf{7}}{\mathrm{Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)HfH_2}} \quad (12)$$

Dihydride **7** has not been isolated cleanly; rather a mixture of **7** and the metallated propyl hydride **8** is obtained from petroleum ether. The equilibrium shown in equation 13 can be driven to the right by the periodic removal of H_2 from the reaction vessel, thus allowing the isolation of clean samples of **8**.



(13)

7 **8**

Introducing dihydrogen into an NMR tube charged with **8** and benzene–d_6 re–establishes the equilibrium shown in equation 13 with detectable concentrations of **7** and **8**. The temperature dependence of the equilibrium (Table 3) indicates $\Delta H^o = +15.5(3)$ kcal mol^{-1} and $\Delta S^o = 33.5(5)$ e.u. for equation 13.

Table 3. Equilibrium constants for the equilibrium between $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)HfH$, dihydrogen, and $Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)HfH_2$ in benzene–d_6 (equation 13).

Temperature (°C)	K_{eq} (x 10^3)
70	3.28
80	3.78
90	9.58
100.5	15.0
114	39.6

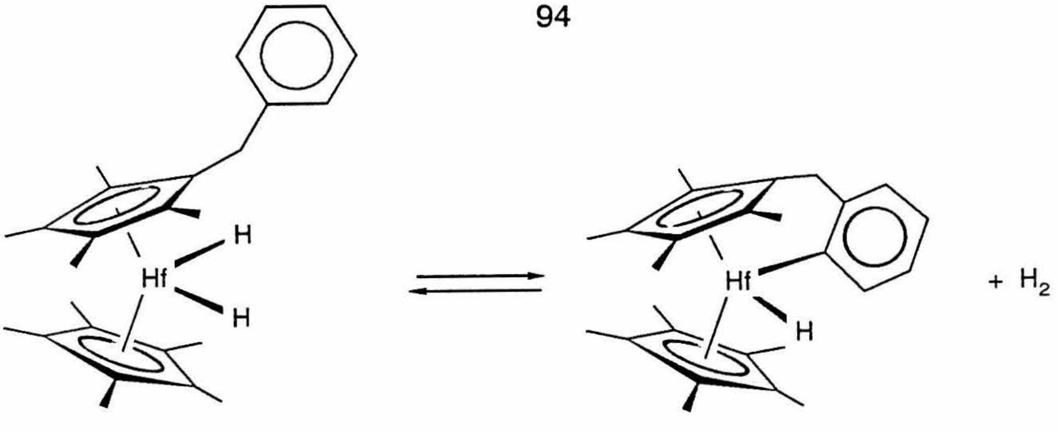
$\Delta H° = +\ 15.5(3)\ \text{kcal}\cdot\text{mol}^{-1}$

$\Delta S° = +\ 33(1)$ e.u.

Relative Hf–aryl and Hf–H BDEs were also determined for comparison to values obtained *via* the intermolecular equilibrations described above. Thus, the metallated benzyltetramethylcyclopentadienyl hafnium hydride complex $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_4)HfH$ has been prepared as shown in equations 14–16.

$$Cp^*HfCl_3 + Li(C_5Me_4CH_2C_6H_5) \xrightarrow[\text{xylenes}]{\text{refluxing}} \underset{\mathbf{9}}{Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)HfCl_2} + LiCl \qquad (14)$$

$$\underset{\mathbf{9}}{Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)HfCl_2} \xrightarrow[\substack{2)\ H_2,\ 80\,°C \\ -\ 2\ C_6H_5CH_3}]{\substack{1)\ 2\ C_6H_5CH_2K \\ -\ 2\ KCl}} \underset{\mathbf{10}}{Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)HfH_2} \qquad (15)$$



(16)

10 **11**

The equilibrium shown in equation 16 is driven to right by the periodic removal of dihyrogen from the reaction vessel. From the temperature dependence of this equilibrium a ΔH° = +8.5(3) kcal · mol^{-1} and a ΔS° = 19(5) e.u. were obtained. The similarity of the enthalpy for equation 16 to that for equation 3 (ΔH° = +6.0(3) kcal · mol^{-1}) suggests only a small ring strain energy for metallation of the benzyl group of the (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_4) ligand.[7]

Table 4. Equilibrium constants for the equilibrium between Cp*(η^5,η^1–$C_5Me_4CH_2C_6H_4$)HfH, dihydrogen, and Cp*(η^5–$C_5Me_4CH_2C_6H_5$)HfH_2 in benzene–d_6 (equation 16).

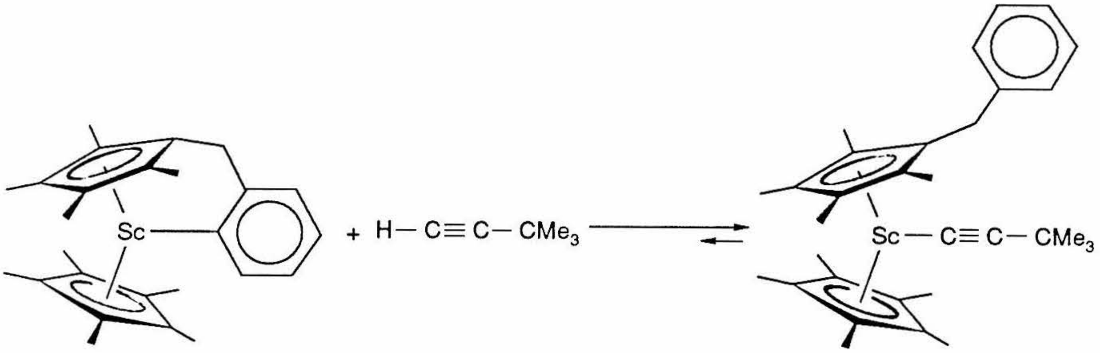
Temperature (°C)	K_{eq} (x 10^2)
59	3.56
73	5.90
86.5	9.60
98.5	17.2
113	19.0
ΔH° = + 8.5(3)	
ΔS° = + 19(1)	

Attempts to equilibrate Sc–aryl and Sc–alkynyl complexes were unsuccessful, presumably due to the exceptionally strong Sc–carbon bonds of the latter. For example, $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_4)Sc$ (**12**), prepared as shown in equations 17 and 18, reacts completely with *tert*–butylacetylene; no detectable amount of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_4)Sc$ remains.

$$[Cp^*ScCl_2]_n + Li^+(C_5Me_4CH_2C_6H_5)^- \longrightarrow Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)ScCl + LiCl \quad (17)$$

$$\begin{tikzcd}
Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)ScCl \arrow[r, "CH_3Li"] & Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)Sc\text{–}CH_3 + LiCl \arrow[d, "- CH_4"] & \\
& \underset{\mathbf{12}}{Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_4)Sc} & (18)
\end{tikzcd}$$

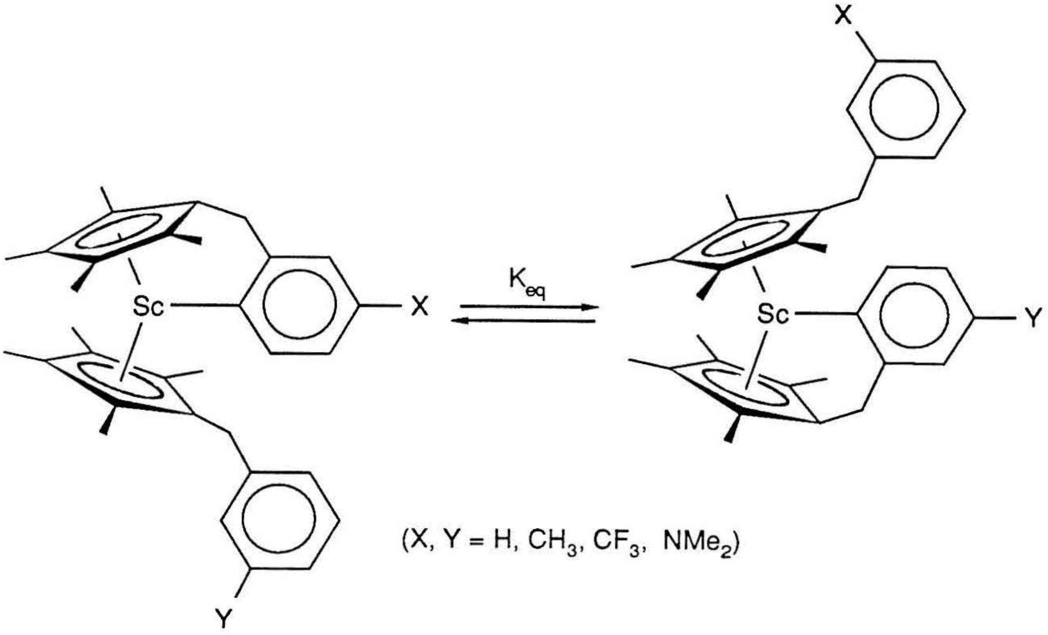
When only 0.5 equivalent of $Me_3CC{\equiv}C\text{–}H$ is used, no free acetylene remains. Thus the equilibrium constant for equation 19 must be greater than $10^2\ M^{-1}$.



(19)

12 **13**

Determination of Aryl Substituent Effects on the Relative Sc–Aryl Bond Dissociation Energies. In order to determine the polarity of the Sc–aryl bond, a series of compounds which can metallate at either of two differently substituted benzyl groups has been prepared (equation 20).



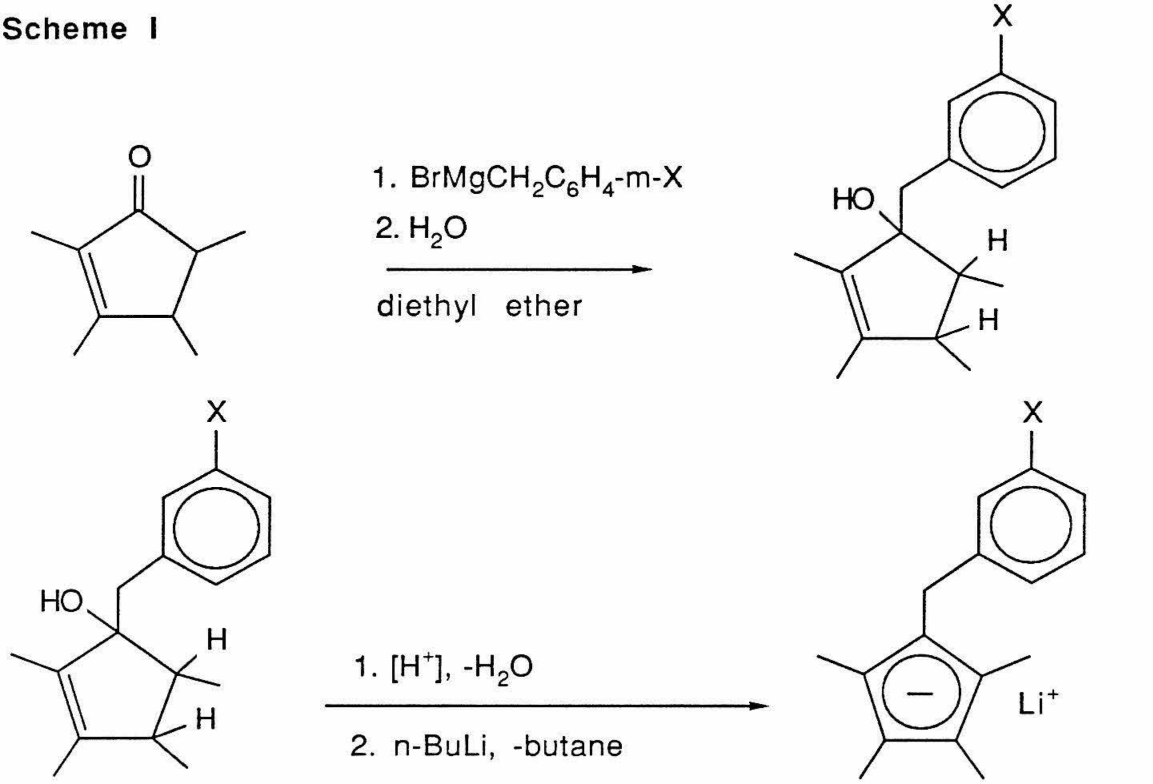
(20)

(X, Y = H, CH_3, CF_3, NMe_2)

Any ionic contribution to the Sc–aryl BDE, and hence, the equilibrium constant, should respond to the electron releasing or electron withdrawing power of the substitutents X and Y.

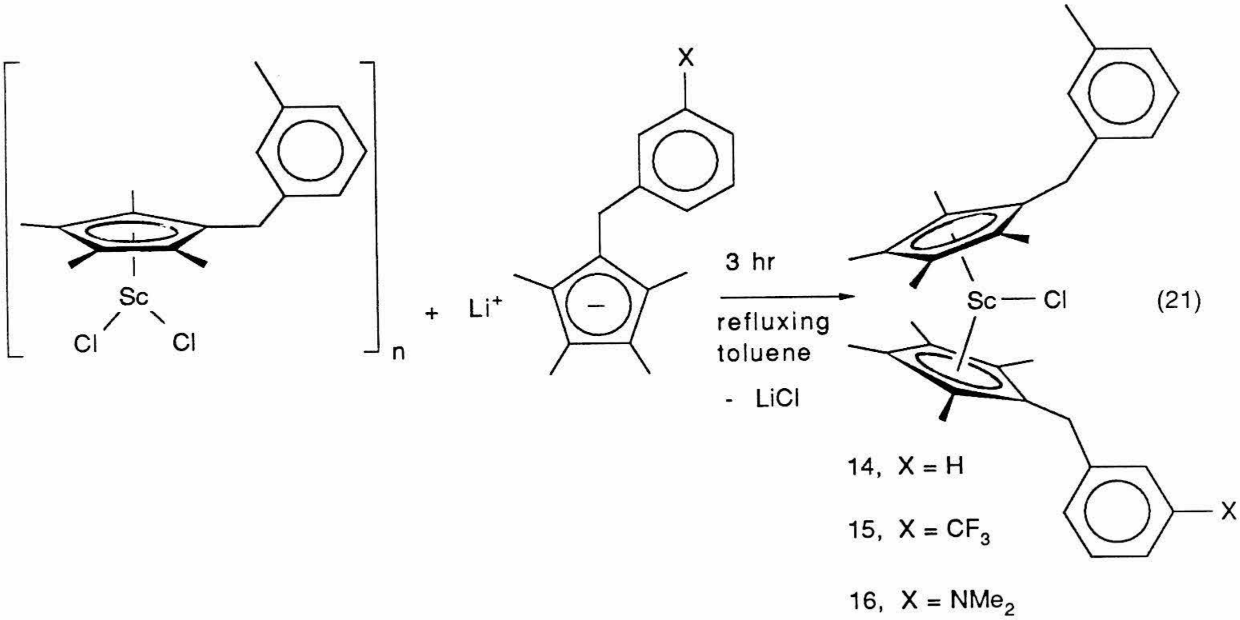
Each of the substituted benzyltetramethylcyclopentadienyl anions has been prepared from the appropriate benzyl Grignard reagent and tetramethylcyclopentenone, followed by dehydration of the resulting alcohol. Treatment of the isomeric mixture of tetramethylbenzylcyclopentadienes with n-butyllithium affords the lithium salt of the anion in moderate yield (Scheme 1).

Scheme I



$X = H, CH_3, NMe_2$, and CF_3

The mixed–Cp scandocene chloride compounds $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_5)ScCl$ (**14**), $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CF_3)ScCl$ (**15**), and $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}NMe_2)ScCl$ (**16**) are prepared by refluxing $\{(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)ScCl_2\}_n$ with the appropriate tetramethylbenzylcyclopentaienyl anion in toluene (equation 21).

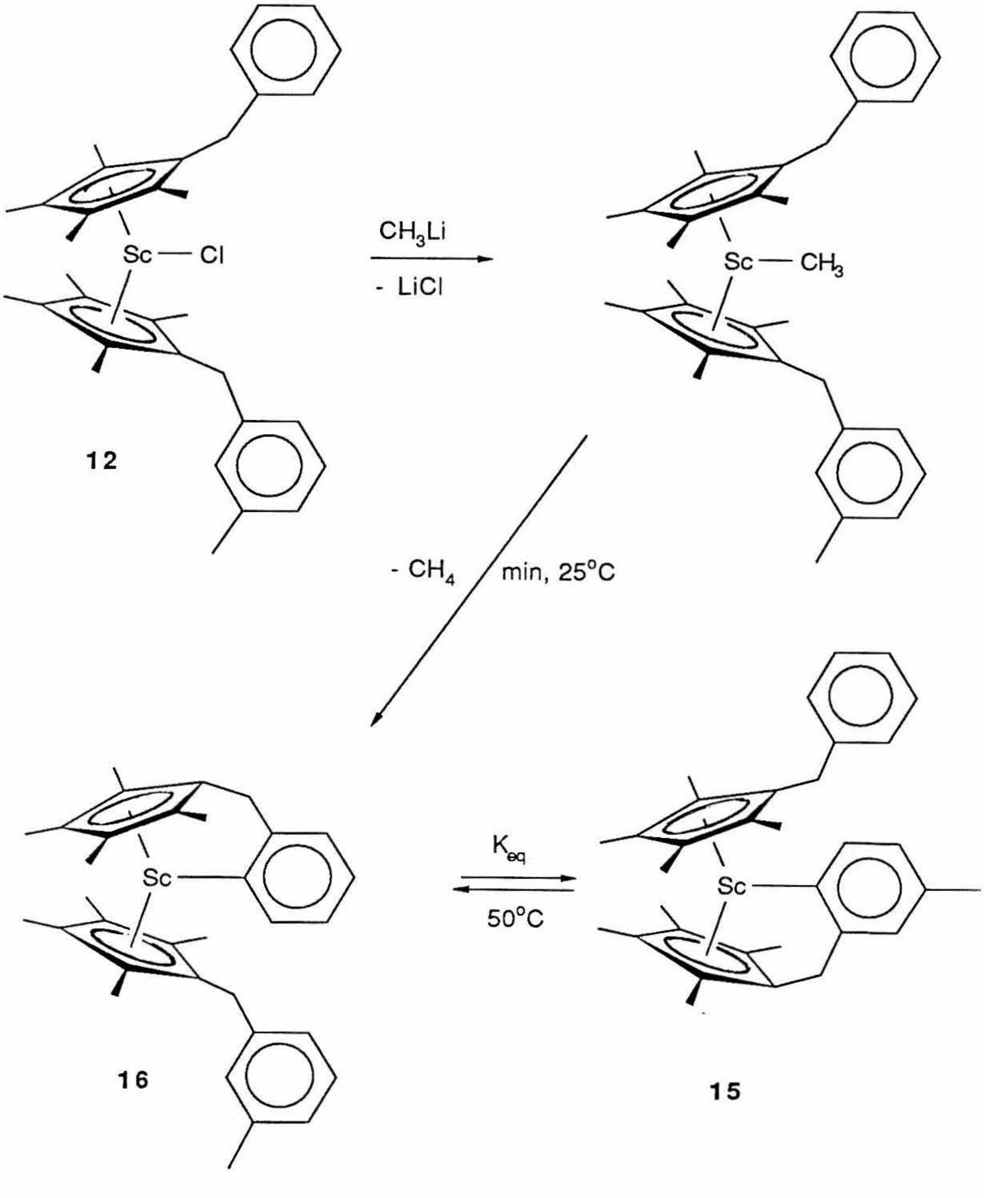


(21)

Since ^{1}H NMR analysis of the equilibrium mixture proved rather complex (even at 500 MHz), we have chosen (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3) as the reference substituted benzyl ligand. When metallated, *e.g.* for Cp*(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)Sc, the (η^5–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3) resonance appears characteristically at δ 2.37. For the compounds described below, this signal consistently shifts from δ 2.05-2.11 to δ 2.37-2.38 on *ortho*–metallation (Table 5), thus serving as a reliable indicator.

Treating the scandium chloride (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_5$)ScCl with one equivalent of methyllithium generates over the course of one hour one equivalent of methane and the isomeric mixture (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)(η^5–$C_5Me_4CH_2C_6H_5$)Sc (**17**) and (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_4)Sc (**18**) in a 1:2 ratio (Scheme 2).

Scheme II



Heating this 1:2 mixture overnight at 110 °C in benzene–d_6 does not alter this ratio. In order to establish that this 1:2 ratio of **17** and **18** is the equilibrium mixture, a small amount of dihydrogen was introduced to catalyze interconversion of **17** and **18**, *via* σ bond metathesis reactions with $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_5)Sc\text{–}H$. Again, no change from the statistical 1:2 ratio is noted.

Treating (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)ScCl with one equivalent of trimethylsilylmethyllithium rapidly generates tetramethylsilane and a *ca.* 1:1 mixture of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CF_3)Sc (**19**) and (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)Sc (**20**), presumably *via* (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)Sc–CH_2SiMe_3. When warmed to 50 °C for a few minutes, the ratio of **19** to **20** changes to 16:1. Continued heating at 50 °C results in decomposition over a period of 1-2 hr; however, the ratio of **18** to **20** remains *ca.* 16:1. A much more thermally robust mixture of **19** and **20** is obtained using an alternative preparation. Treating (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)ScCl with one equivalent of phenyllithium generates the phenyl derivative (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)Sc–C_6H_5, which is stable to loss of benzene at ambient temperature. Heating an isolated sample of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)Sc–C_6H_5 in benzene–d_6 to 80 °C results in benzene loss and the 16:1 isomeric mixture[8] of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CF_3)Sc (**19**) and (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)Sc (**20**). Thermal decomposition of this mixture is much slower, requiring several days at 80 °C. The variable thermal stabilities of these compounds from batch to batch suggests decomposition is catalyzed by trace impurities, but the value of K_{eq} is not in doubt (**19** $\rightleftharpoons$ **20**, K_{eq} = 0.063(6))

Treating (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–NMe_2)ScCl with one equivalent of LiC_6H_5 cleanly generates (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–NMe_2)ScC_6H_5. This complex has not been isolated, rather it is generated *in situ* and characterized by ^{1}H NMR. Heating benzene–d_6 solutions of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–NMe_2)ScC_6H_5 overnight at 50 °C generates C_6H_6 and a 1:1 mixture of $(\eta^5.\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_3\text{–}p\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}NMe_2)Sc$ (**21**) and $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_3\text{–}p\text{–}NMe_2)Sc$ (**22**). As with X=H and CH_3, heating solutions of the initially formed mixture at 80 °C for several hours does not alter the isomeric ratio (nor does it effect decomposition). In order to assure that a true thermodynamic equilibrium had been reached, once again a small amount of dihydrogen was introduced into a benzene–d_6 solution of the phenyl derivative $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}NMe_2)Sc\text{–}C_6H_5$ to catalyze rapid interconversion of **21** and **22** *via* $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}NMe_2)Sc\text{–}H$. After heating for 20 hr at 50 °C no deviation from the original 1:1 ratio of $(\eta^5.\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_3\text{–}p\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}NMe_2)Sc$ (**21**) and $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_4\text{–}p\text{–}NMe_2)Sc$ (**22**) was noted. Thus, as for **17** and **18** no detectable substituent effect of the equilibrium constant for the two isomeric metallated benzyl complexes **21** and **22** obtains.

Discussion

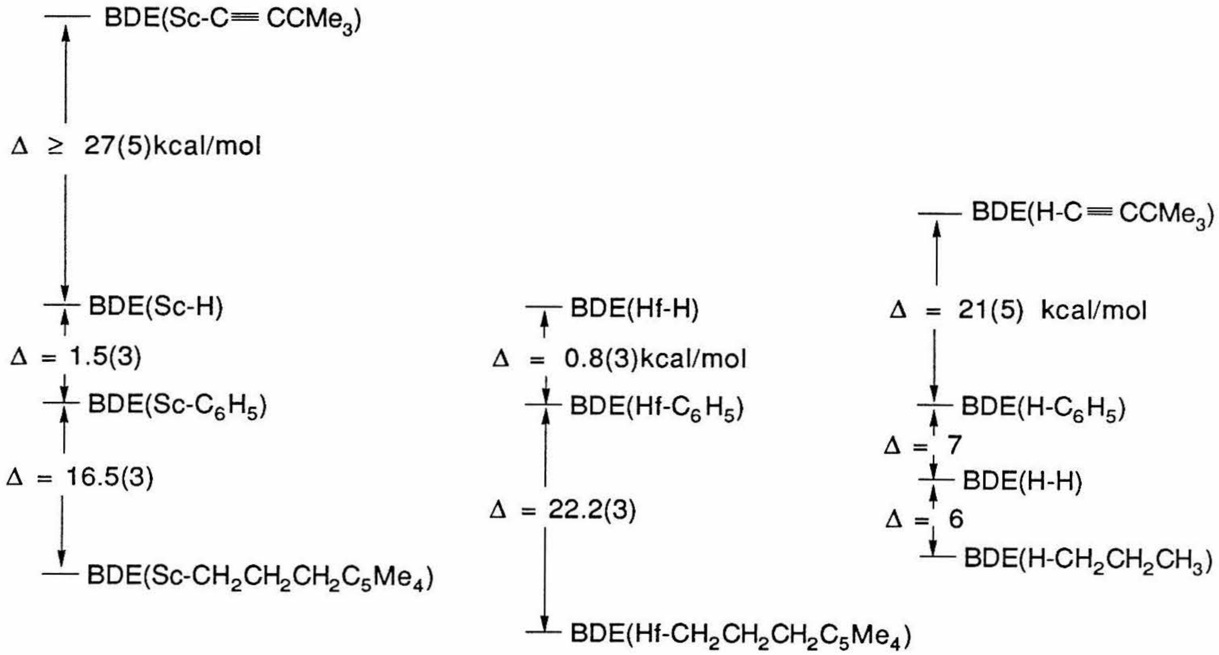
Sigma bond metathesis has proven to be a convenient method to obtain information on the relative bond dissociation energies for these types of transition metal hydrides and hydrocarbyls. Due to interfering reactions, mostly likely involving the C–H bonds of the $(\eta^5\text{–}C_5Me_5)$ ligands, *inter*molecular equilibrations appear to be limited to the very stable hydride and phenyl derivatives. Although our data indicate that the alkynyl complexes are even more stable, side reactions such as catalytic dimerization of terminal acetylenes to *gem*–enynes[7] preclude equilibration.

By incorporating reactive groups into the cyclopentadienyl ligands and introducing systematic variations we have capitalized on the tendency for the ligand C–H bonds to participate in the σ bond metathesis reactions. Moreover, the favorable entropy associated with these intramolecular metallation reactions ($\Delta S^o = 11 - 34$ e.u.) provides an additional driving force ($T\Delta S^o = 3 - 10\ \mathrm{kcal \cdot mol^{-1}}$ at ambient temperature) to shift otherwise prohibitively endothermic equilibria to allow the concentrations of all participants to be accurately determined. These equilibrium constants (*e.g.* equations 8, 13, and 16) are no longer unitless, so that the issue of standard states[9] and transferability of K_{eq}'s or ΔG°'s is potentially problematic. However, by comparing ΔH^o values obtained from the temperature dependence of the equilibrium constants, we can draw some meaningful comparisons. Another point of possible concern is the introduction of ring strain on metallation. Models suggest, and experiments appear to bear out (*e.g.* compare ΔH^o values for equations 3 and 16) that there is little strain for a three-carbon link connecting the cyclopentadienyl ring carbon atom and the metal center. In the final series of experiments, those involving competitive metallation by scandium at either of two benzyl-substituted cyclopentadienyl ligands, the symmetry of the ligand system and the fact that the equilibrium constants are unitless eliminates these concerns completely.

The enthalpies of the equilibrium, established by these sigma bond metathesis reactions (equation 1), allow the relative M–R and M–R' bond strengths to be determined if one assumes the Benson approximation[10] and cancellation of the solvation energies[11,12]. In equation 3, for example, since the H–C_6H_5 BDE = 110.9 $\mathrm{kcal \cdot mol^{-1}}$[13], H–H BDE = 104.2 $\mathrm{kcal \cdot mol^{-1}}$[14] and the heat of solvation of H_2 in benzene = –1.5 $\mathrm{kcal \cdot mol^{-1}}$[15], then the +6.0(3) $\mathrm{kcal \cdot mol^{-1}}$ enthalpy of reaction indicates the BDE(Hf–H) is greater than BDE(Hf–C_6H_5) by (104.2 – 110.9 + 1.5 +6.0) = 0.8(3) $\mathrm{kcal \cdot mol^{-1}}$. In equation 8, if the C–H BDE for $Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_2\text{–}H)Sc\text{–}C_6H_5$ is assumed to be 98 $\mathrm{kcal \cdot mol^{-1}}$ (the BDE for the 1° C–H bonds of propane), then the

BDE($Sc-C_6H_5$) is greater than BDE($Sc-CH_2CH_2CH_2C_5Me_4$) by 16.6(3) kcal · mol^{-1}, since BDE($H-C_6H_5$) = 110.9 kcal · mol^{-1} and ΔH^o = +3.7(3) kcal · mol^{-1}. The following ordering for Hf–R and Sc–R BDEs are calculated in an analogous manner (Scheme 3):

Scheme III



Whereas the differences in metal–hydride and metal–phenyl bond strengths are essentially the same for Sc and Hf, the same cannot be said for the metal–phenyl *vs.* metal–$CH_2CH_2CH_2C_5Me_4$ bond strengths. Some of the *ca.* 6 kcal · mol^{-1} discrepancy may be due to different ring strain energies for the pseudo trigonal scandium *vs.* pseudotetrahedral hafnium. On the other hand, the total strain energy for the hafnium derivative amounts to only *ca.* 2.5(3) kcal · mol^{-1}, since according to equilibrium 16, the BDE(Hf–H) is greater than BDE($Hf-C_6H_4CH_2C_5Me_4$) by 3.3(3) kcal · mol^{-1}. Whatever the sources of these small effects, some general conclusions can be derived from the differences in bond strengths as the hybridization at the α carbon is varied. The order of decreasing BDEs is M–C(sp) > M–C(aryl) > M–C(sp^3), the same order as for H–C BDEs for hydrocarbons. However, the relative differences for hydrogen–carbon bond strengths is smaller $\{$BDE[H–C(sp)] = 132(5); BDE[H–C(aryl)] = 111; BDE[H–C(1^o,sp^3)] = 98 kcal · mol$^{-1}\}$ than those for the hafnium and scandium hydrocarbyls. Indeed, if the relative differences were the same, these equilibria would be essentially thermoneutral (*i.e.* $\Delta H^o \approx 0$). Additional, qualitative evidence which supports this point is provided by the intramolecular equilibration of $(\eta^5,\eta^1\text{–}C_5Me_4CH_2\text{–}o\text{–}C_6H_3\text{–}p\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)Sc$ (**5**) with $(\eta^5\text{–}C_5Me_4CH_2C_6H_3\text{–}m\text{–}CH_3)(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)Sc$; the Sc–aryl isomer **5** being strongly favored. The origin of the effect which is responsible for the M–R BDEs increasing more rapidly with s character than do the H–R BDEs is not clear; however, it undoubtedly also results in stronger M–H BDEs than would be anticipated on the basis of the correlation suggested by Bryndza, Bercaw and co-workers.[11,16] For these early transition metal hydride compounds the BDE(M–H) is *ca.* 8 kcal · mol^{-1} stronger than this correlation predicts.

The sensitivity of the transition metal–carbon bond energy to s character could be a reflection of considerable ionic ($M^{\delta+}\text{–}C^{\delta-}$) bonding, since s character at carbon increases its electronegativity. The experiments designed to probe this aspect of the Sc–aryl bonding, equilibria 20, reveal very little substituent effect on the Sc–aryl BDE[17]. Only for *para*–CF_3 is a measureable difference obtained. *Para*–NMe_2 exerts its effect primarily through resonant π donation. Interestingly, the phenyl ring is held perpendicular to the equatorial plane of the scandocene moiety by the link to the cyclopentadienyl ligand, *i.e.* in resonance with the empty π symmetry (b_2) scandium orbital. Thus, resonant donation is possible, but apparently is cancelled by the small inductive withdrawing character of the electronegative N atom. The generally small effect observed, even with the strongly withdrawing CF_3

substituent, is quite significant, and dictates that there is little polarity for the Sc–C bond in these compounds. These experimental results are in generally in accord with the picture presented by Goddard and Steigerwald[18] for the scandium–hydride of $Cl_2Sc–H$, for which the electronegative Cl ligands (and by extension the Cp* ligands) bond primarily *via* the Sc 4s orbitals, with the Sc–H bonding being 3d–1s in character and essentially covalent. It appears this same 3d character also dominates the Sc orbital used in the Sc–aryl bonding of compounds **17** – **22.**

Table 5. ^{1}H and ^{13}C NMR Data [a].

Compound	Assignment	δ (ppm)	Coupling[b]
$\mathrm{Li^+(C_5Me_4CH_2C_6H_4}$-*m*-$\mathrm{CH_3)^-}$ [c]			
	η^5-$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_4CH_2C_6H_4}$-*m*-$\mathrm{CH_3}$	1.87 s	
	η^5-$\mathrm{C_5(CH_3)_4C}\mathit{H}\mathrm{_2C_6H_4}$-*m*-$\mathrm{CH_3}$	3.63 br	
	η^5-$\mathrm{C_5(CH_3)_4CH_2C_6H_4}$-*m*-$\mathrm{C}\mathit{H}\mathrm{_3}$	2.20 s	
	η^5-$\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}\mathrm{_4}$-*m*-$\mathrm{CH_3}$	6.6-7.0 m	
$\mathrm{Li^+(C_5Me_4CH_2C_6H_4}$-*m*-$\mathrm{CF_3)^-}$ [c]			
	η^5-$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_4CH_2C_6H_4}$-*m*-$\mathrm{CF_3}$	1.83 s	
		1.87 s	
	η^5-$\mathrm{C_5(CH_3)_4C}\mathit{H}\mathrm{_2C_6H_4}$-*m*-$\mathrm{CF_3}$	3.80 br	
	η^5-$\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}\mathrm{_4}$-*m*-$\mathrm{CF_3}$	7.1-7.4 m	
$\mathrm{Li^+(C_5Me_4CH_2C_6H_4}$-*m*-$\mathrm{N(CH_3)_2)^-}$ [c]			
	η^5-$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_4CH_2C_6H_4}$-*m*-$\mathrm{N(CH_3)_2}$	1.93 s	
		1.90 s	
	η^5-$\mathrm{C_5(CH_3)_4C}\mathit{H}\mathrm{_2C_6H_4}$-*m*-$\mathrm{N(CH_3)_2}$	3.60 br	
	η^5-$\mathrm{C_5(CH_3)_4CH_2C_6H_4}$-*m*-$\mathrm{N(C}\mathit{H}\mathrm{_3)_2}$	2.80 s	
	η^5-$\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}\mathrm{_4}$-*m*-$\mathrm{N(CH_3)_2}$	6.3-7.0 m	
Cp*(η^5-$\mathrm{C_5Me_4CH_2CH_2CH_3}$)ScCl (1)			
	η^5-$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_5}$	1.90 s	
	η^5-$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_4CH_2CH_2CH_3)}$	1.85 s	
		2.01 s	
	η^5-$\mathrm{C_5Me_4CH_2CH_2C}\mathit{H}\mathrm{_3}$	0.79 t	$^3J_{HH} = 7$
	η^5-$\mathrm{C_5Me_4CH_2C}\mathit{H}\mathrm{_2CH_3}$	1.24 m	$^3J_{HH} = 7$
	η^5-$\mathrm{C_5Me_4C}\mathit{H}\mathrm{_2CH_2CH_3}$	2.35 t	$^3J_{HH} = 7$
Cp*(η^5,η^1-$\mathrm{C_5Me_4CH_2CH_2CH_2}$)Sc (2)			
	η^5-$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_5}$	1.83 s	
	η^5,η^1-$\mathrm{C_5(C}\mathit{H}\mathrm{_3)_4CH_2CH_2CH_2}$	1.57 s	
		1.97 s	
	η^5,η^1-$\mathrm{C_5Me_4CH_2CH_2C}\mathit{H}\mathrm{_2}$	0.77 t	$^3J_{HH} = 6.6$
	η^5,η^1-$\mathrm{C_5Me_4CH_2C}\mathit{H}\mathrm{_2CH_2}$	2.73 tt	$^3J_{HH} = 6.6$
	η^5,η^1-$\mathrm{C_5Me_4C}\mathit{H}\mathrm{_2CH_2CH_2}$	2.91 t	$^3J_{HH} = 6.6$
	η^5-$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	11.40 q	$^1J_{CH} = 126$
	η^5-$\mathit{C}\mathrm{_5(CH_3)_5}$	119.4 s	
	η^5,η^1-$\mathrm{C_5Me_4CH_2CH_2}\mathit{C}\mathrm{H_2}$	*not observed*	
	η^5,η^1-$\mathrm{C_5Me_4CH_2}\mathit{C}\mathrm{H_2CH_2}$	38.76 t	$^1J_{CH} = 120$
	η^5,η^1-$\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2CH_2CH_2}$	28.9 t	$^1J_{CH} = 123$
	η^5,η^1-$\mathit{C}\mathrm{_5(CH_3)_4CH_2CH_2CH_2}$	117.0 s	
		119.6 s	
		138.2 s	

$Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH_3)Sc(C_6H_5)$ (3)[f]

$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.68 s	
$\eta^5\text{-}C_5(C\mathit{H}_3)_4CH_2CH_2CH_3)$	1.70 s	
	1.72 s	
$\eta^5\text{-}C_5Me_4CH_2CH_2C\mathit{H}_3$	0.82 t	$^3J_{HH} = 7$
$\eta^5\text{-}C_5Me_4CH_2C\mathit{H}_2CH_3$	1.22 m	$^3J_{HH} = 7$
$\eta^5\text{-}C_5Me_4C\mathit{H}_2CH_2CH_3$	2.18 t	$^3J_{HH} = 7$
$Sc(C_6\mathit{H}_5)$	6.81 d	$^3J_{HH} = 7$
	6.95 t	$^3J_{HH} = 7$
	7.09 t	$^3J_{HH} = 7$

$(\eta^5\text{-}C_5Me_4CH_2C_6H_4\text{-}m\text{-}CH_3)(\eta^5\text{-}C_5Me_4CH_2CH_2CH_3)ScCl$ (4)

$\eta^5\text{-}C_5(C\mathit{H}_3)_4CH_2C_6H_4\text{-}m\text{-}CH_3$	1.85 s	
$\eta^5\text{-}C_5(C\mathit{H}_3)_4CH_2CH_2CH_3$	1.88 s	
	1.98 s	
	2.05 s	
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6H_4\text{-}m\text{-}C\mathit{H}_3$	2.11 s	
$\eta^5\text{-}C_5(CH_3)_4C\mathit{H}_2C_6H_4\text{-}m\text{-}CH_3$	3.79 b	
$\eta^5\text{-}C_5(CH_3)_4C\mathit{H}_2CH_2CH_3$	2.33 t	$^3J_{HH} = 8$
$\eta^5\text{-}C_5(CH_3)_4CH_2C\mathit{H}_2CH_3$	1.24 tq	$^3J_{HH} = 8$
$\eta^5\text{-}C_5(CH_3)_4CH_2CH_2C\mathit{H}_3$	0.81 t	$^3J_{HH} = 8$
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6\mathit{H}_4\text{-}m\text{-}CH_3$	6.81-7.08 m	

$(\eta^5\text{-}C_5Me_4CH_2CH_2CH_3)(\eta^5,\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CH_3)Sc$ (5)[g]

$\eta^5,\eta^1\text{-}C_5(C\mathit{H}_3)_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CH_3$	1.53 s	
$\eta^5\text{-}C_5(C\mathit{H}_3)_4CH_2CH_2CH_3$	2.02 s	
	2.08 s	
	2.17 s	
$\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}C\mathit{H}_3$	2.20 s	
$\eta^5,\eta^1\text{-}C_5(CH_3)_4C\mathit{H}_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CH_3$	3.86 b	
$\eta^5\text{-}C_5(CH_3)_4C\mathit{H}_2CH_2CH_3$	2.50 t	$^3J_{HH} = 7$
$\eta^5\text{-}C_5(CH_3)_4CH_2C\mathit{H}_2CH_3$	1.29 tq	$^3J_{HH} = 7$
$\eta^5\text{-}C_5(CH_3)_4CH_2CH_2C\mathit{H}_3$	0.87 t	$^3J_{HH} = 7$
$\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2\text{-}o\text{-}C_6\mathit{H}_3\text{-}p\text{-}CH_3$	6.94 s	
	6.70 d	$^3J_{HH} = 8$
	8.05 d	$^3J_{HH} = 8$

$Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH_3)HfCl_2$ (6)

$\eta^5\text{-}C_5(C\mathit{H}_3)_5$	1.93 s	
$\eta^5\text{-}C_5(C\mathit{H}_3)_4CH_2CH_2CH_3$	1.91 s	
	1.99 s	
$\eta^5\text{-}C_5Me_4CH_2CH_2C\mathit{H}_3$	0.82 t	$^3J_{HH} = 7.3$
$\eta^5\text{-}C_5Me_4CH_2C\mathit{H}_2CH_3$	1.28 m	$^3J_{HH} \sim 8$
$\eta^5\text{-}C_5Me_4C\mathit{H}_2CH_2CH_3$	2.50 t	$^3J_{HH} = 8.0$

Cp*(η^5-$\mathrm{C_5Me_4CH_2CH_2CH_3}$)$\mathrm{HfH_2}$ (7)

η^5-$\mathrm{C_5(C}H_3\mathrm{)_5}$	2.07 s	
η^5-$\mathrm{C_5(C}H_3\mathrm{)_4CH_2CH_2CH_3}$	2.10 s	
	1.92 s	
η^5-$\mathrm{C_5Me_4CH_2CH_2C}H_3$	0.88 t	$^3J_{HH} = 8$
η^5-$\mathrm{C_5Me_4CH_2C}H_2\mathrm{CH_3}$	1.41 m	$^3J_{HH} = 8$
η^5-$\mathrm{C_5Me_4C}H_2\mathrm{CH_2CH_3}$	2.50 t	$^3J_{HH} = 8$
$\mathrm{Hf}H_2$	15.6	

Cp*(η^5,η^1-$\mathrm{C_5Me_4CH_2CH_2CH_2}$)HfH (8)

η^5-$\mathrm{C_5(C}H_3\mathrm{)_5}$	1.91 s	
η^5,η^1-$\mathrm{C_5(C}H_3\mathrm{)_4CH_2CH_2CH_2}$	1.68 s	
	1.70 s	
	1.72 s	
	2.64 s	
η^5,η^1-$\mathrm{C_5Me_4C}H_2\mathrm{C}H_2\mathrm{C}H_2$	-0.60 m	
	0.31 m	
	1.90 m	
	2.02 m	
	2.58 m	
	2.78 m	
$\mathrm{Hf}H$	13.2	

η^5,η^1-$\mathrm{C_5(CH_3)_4(CH_2CH_2}C\mathrm{H_2)}$	74.09 t	
η^5,η^1-$\mathrm{C_5(CH_3)_4(CH_2}C\mathrm{H_2CH_2)}$	37.58 t	$^1J_{CH} = 125$
η^5,η^1-$\mathrm{C_5(CH_3)_4(}C\mathrm{H_2CH_2CH_2)}$	27.28 t	$^1J_{CH} = 120$

Cp*(η^5-$\mathrm{C_5Me_4CH_2C_6H_5}$)$\mathrm{HfCl_2}$ (9)[d]

η^5-$\mathrm{C_5(C}H_3\mathrm{)_5}$	2.03 s	
η^5-$\mathrm{C_5(C}H_3\mathrm{)_4CH_2C_6H_5}$	1.97 s	
	2.03 s	
η^5-$\mathrm{C_5(CH_3)_4C}H_2\mathrm{C_6H_5}$	3.80 br	
η^5-$\mathrm{C_5(CH_3)_4CH_2C_6}H_5$	6.9-7.2 m	

Cp*(η^5-$\mathrm{C_5Me_4CH_2C_6H_4}$-*m*-$\mathrm{CH_3}$)$\mathrm{Hf(CH_2C_6H_5)_2}$ [e]

η^5-$\mathrm{C_5(C}H_3\mathrm{)_5}$	1.75 s	
η^5-$\mathrm{C_5(C}H_3\mathrm{)_4CH_2C_6H_5}$	1.74 s	
	1.76 s	
η^5-$\mathrm{C_5(CH_3)_4C}H_2\mathrm{C_6H_5}$	3.61 br	
$\mathrm{HfC}H_2\mathrm{C_6H_5}$	1.44 d	$^2J_{HH} = 13$
	1.49 d	$^2J_{HH} = 13$
η^5-$\mathrm{C_5(CH_3)_4CH_2C_6}H_5$	6.9-7.2 m	
$\mathrm{HfCH_2C_6}H_5$	6.9-7.2 m	

Cp*(η^5-$\mathrm{C_5Me_4CH_2C_6H_5}$)$\mathrm{HfH_2}$ (10)

η^5-$\mathrm{C_5(C}H_3\mathrm{)_5}$	2.07 s	
η^5-$\mathrm{C_5(C}H_3\mathrm{)_4CH_2C_6H_5}$	1.97 s	

η^5-$C_5(CH_3)_4CH_2C_6H_5$	7.0-7.2 m	
Hf-H	15.70	

Cp*(η^5,η^1-$C_5Me_4CH_2$-o-C_6H_4)HfH (11)

η^5-$C_5(CH_3)_5$	1.95 s	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_4	1.74 s	
	1.87 s	
	1.97 s	
	2.02 s	
η^5,η^1-$C_5Me_4CH_2$-o-C_6H_4	3.76 d	$^2J_{HH}$ = 17
	3.92 d	$^2J_{HH}$ = 17
η^5,η^1-$C_5Me_4CH_2$-o-C_6H_5	7.2-7.5 m	
Hf-H	14.15 br	

Cp*(η^5,η^1-$C_5Me_4CH_2$-o-C_6H_3-p-CH_3)Sc [g]

η^5-$C_5(CH_3)_5$	1.96 s	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_3-p-CH_3	2.03 s	
	1.48 s	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_3-p-CH_3	2.37 s	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_3-p-CH_3	4.06 br	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_3-p-CH_3	8.45 d	$^3J_{HH}$ = 7.4
	7.13 d	$^3J_{HH}$ = 7.4
	7.26 br	

Cp*(η^5-$C_5Me_4CH_2C_6H_5$)ScCl [e]

η^5-$C_5(CH_3)_5$	1.88 s (7 methyls)	
η^5-$C_5(CH_3)_4CH_2C_6H_4$	1.97 s (2 methyls)	
η^5-$C_5(CH_3)_4CH_2C_6H_4$	3.75 br	
η^5-$C_5(CH_3)_4CH_2C_6H_4$	7.0-7.2 m	

Cp*(η^5,η^1-$C_5Me_4CH_2$-o-C_6H_4)Sc (12)[g]

η^5-$C_5(CH_3)_5$	1.95 s	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_4	2.01 s	
	1.45 s	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_4	4.08 br	
η^5,η^1-$C_5(CH_3)_4CH_2$-o-C_6H_4	7.3-8.55 m	

Cp*(η^5-$C_5Me_4CH_2C_6H_5$)Sc-C≡CMe_3 (13)

η^5-$C_5(CH_3)_5$	1.88 s	
η^5-$C_5(CH_3)_4CH_2C_6H_4$	1.97 s	
	2.07 s	
$C(CH_3)_3$	1.30 s	
η^5-$C_5(CH_3)_4CH_2C_6H_4$	3.73 br	
η^5-$C_5(CH_3)_4CH_2C_6H_4$	7.0-7.3 m	

$(\eta^5\text{-}\mathrm{C_5Me_4CH_2C_6H_5})\mathrm{Sc(acac)_2}$ [d]

$\eta^5\text{-}\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2C_6H_5}$	1.87 s
	1.90 s
$\eta^2\text{-}\mathrm{OC(C}\mathit{H}_3\mathrm{)CH(C}\mathit{H}_3\mathrm{)CO}$	2.03 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4C}\mathit{H}_2\mathrm{C_6H_5}$	3.73 br
$\eta^2\text{-}\mathrm{OC(CH_3)C}\mathit{H}\mathrm{(CH_3)CO}$	5.57 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}_5$	7.0-7.3 m

$(\eta^5\text{-}\mathrm{C_5Me_4CH_2C_6H_5})\mathrm{ScCl_2}$ [c]

$\eta^5\text{-}\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2C_6H_5}$	2.03 s
	2.09 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4C}\mathit{H}_2\mathrm{C_6H_5}$	4.0 br
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}_5$	6.9-7.2 m

$(\eta^5\text{-}\mathrm{C_5Me_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3})(\eta^5\text{-}\mathrm{C_5Me_4CH_2C_6H_5})\mathrm{ScCl}$ (14)

$\eta^5\text{-}\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	1.85 s (2 methyls)
and	
$\eta^5\text{-}\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2C_6H_5}$	1.95 s (1 methyl)
	2.03 s (1 methyl)
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{C}\mathit{H}_3$	2.11 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4C}\mathit{H}_2\mathrm{C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	3.70 br
$\eta^5\text{-}\mathrm{C_5(CH_3)_4C}\mathit{H}_2\mathrm{C_6H_5}$	3.70 br
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}_4\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	6.8-7.2 m
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}_5$	

$(\eta^5\text{-}\mathrm{C_5Me_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3})(\eta^5\text{-}\mathrm{C_5Me_4CH_2C_6H_5})\mathrm{ScH}$

$\eta^5\text{-}\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	1.89 s
and	
$\eta^5\text{-}\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2C_6H_5}$	1.90 s
	2.02 s
	2.06 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{C}\mathit{H}_3$	2.09 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4C}\mathit{H}_2\mathrm{C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	3.79 br
$\eta^5\text{-}\mathrm{C_5(CH_3)_4C}\mathit{H}_2\mathrm{C_6H_5}$	3.79 br
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}_4\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	
and	6.8-7.2 m
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}_5$	

$(\eta^5\text{-}\mathrm{C_5Me_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3})\mathrm{Sc(acac)_2}$ [d]

$\eta^5\text{-}\mathrm{C_5(C}\mathit{H}_3\mathrm{)_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	1.87 s
	1.90 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{C}\mathit{H}_3$	2.27 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4C}\mathit{H}_2\mathrm{C_6H_4}\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	3.70 br
$\eta^2\text{-}\mathrm{OC(C}\mathit{H}_3\mathrm{)CH(C}\mathit{H}_3\mathrm{)CO}$	2.05 s
$\eta^2\text{-}\mathrm{OC(CH_3)C}\mathit{H}\mathrm{(CH_3)CO}$	5.55 s
$\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C_6}\mathit{H}_4\text{-}\mathit{m}\text{-}\mathrm{CH_3}$	6.8-7.3 m

$(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3)\text{ScCl}_2$ [e]

$\eta^5\text{-C}_5(\text{C}\mathit{H}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	2.20 s
	2.28 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-C}\mathit{H}_3$	2.07 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}\mathit{H}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	4.33 br
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\mathit{H}_4\text{-}\mathit{m}\text{-CH}_3$	6.8-7.1 m

$(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3)(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CF}_3)\text{ScCl}$ (15)

$\eta^5\text{-C}_5(\text{C}\mathit{H}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CF}_3$	1.80 s
and	
$\eta^5\text{-C}_5(\text{C}\mathit{H}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	1.82 s
	1.85 s
	2.03 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-C}\mathit{H}_3$	2.08 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}\mathit{H}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	3.72 br
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}\mathit{H}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CF}_3$	3.72 br
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\mathit{H}_4\text{-}\mathit{m}\text{-CH}_3$ and $\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\mathit{H}_4\text{-}\mathit{m}\text{-CF}_3$	6.8–7.4 m

$(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3)(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CF}_3)\text{ScC}_6\text{H}_5$

$\eta^5\text{-C}_5(\text{C}\mathit{H}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	1.63 s
and	
$\eta^5\text{-C}_5(\text{C}\mathit{H}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CF}_3$	1.750 s
	1.758 s
	1.761 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-C}\mathit{H}_3$	2.07 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}\mathit{H}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	3.45 br
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}\mathit{H}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CF}_3$	3.58 br
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\mathit{H}_4\text{-}\mathit{m}\text{-CH}_3$ $\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\mathit{H}_4\text{-}\mathit{m}\text{-CF}_3$ $\text{Sc–C}_6\mathit{H}_5$	6.7-7.5 m

$(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3)(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-NMe}_2)\text{ScCl}$ (16)[g]

$\eta^5\text{-C}_5(\text{C}\mathit{H}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-NMe}_2$	1.86 s
and	
$\eta^5\text{-C}_5(\text{C}\mathit{H}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	1.89 s
	1.97 s
	2.21 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-C}\mathit{H}_3$	2.09 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-N}(\text{C}\mathit{H}_3)_2$	2.59 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}\mathit{H}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-N}(\text{CH}_3)_2$	3.63 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}\mathit{H}_2\text{C}_6\text{H}_4\text{-}\mathit{m}\text{-CH}_3$	3.70 s
$\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\mathit{H}_4\text{-}\mathit{m}\text{-CH}_3$ and $\eta^5\text{-C}_5(\text{CH}_3)_4\text{CH}_2\text{C}_6\mathit{H}_4\text{-}\mathit{m}\text{-N}(\text{CH}_3)_2$	6.4-7.2 m

$(\eta^5\text{-}C_5Me_4CH_2C_6H_4\text{-}m\text{-}CH_3)(\eta^5\text{-}C_5Me_4CH_2C_6H_4\text{-}m\text{-}NMe_2)ScC_6H_5$ [g]

$\eta^5\text{-}C_5(\mathit{CH}_3)_4CH_2C_6H_4\text{-}m\text{-}CH_3$	1.787 s
and	
$\eta^5\text{-}C_5(\mathit{CH}_3)_4CH_2C_6H_4\text{-}m\text{-}NMe_2$	1.792 s
	1.796 s
	1.86 s
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6H_4\text{-}m\text{-}\mathit{CH}_3$	2.06 s
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6H_4\text{-}m\text{-}N(\mathit{CH}_3)_2$	2.51 s
$\eta^5\text{-}C_5(CH_3)_4\mathit{CH}_2C_6H_4\text{-}m\text{-}CH_3$	3.62 br, s
$\eta^5\text{-}C_5(CH_3)_4\mathit{CH}_2C_6H_4\text{-}m\text{-}NMe_2$	3.70
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6\mathit{H}_4\text{-}m\text{-}CH_3$	
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6\mathit{H}_4\text{-}m\text{-}NMe_2$	6.5–7.5 m
$Sc–C_6\mathit{H}_5$	

$(\eta^5\text{-}C_5Me_4CH_2C_6H_5)(\eta^5,\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CH_3)Sc$ (17) [g]

$\eta^5,\eta^1\text{-}C_5(\mathit{CH}_3)_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CH_3$	1.53 s
and	
$\eta^5\text{-}C_5(\mathit{CH}_3)_4CH_2C_6H_5$	1.96 s
	1.993 s
	1.998 s
$\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}\mathit{CH}_3$	2.38 s
$\eta^5\text{-}C_5(CH_3)_4\mathit{CH}_2C_6H_5$	3.90 br, s
$\eta^5,\eta^1\text{-}C_5(CH_3)_4\mathit{CH}_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CH_3$	4.09 br, s
$\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2\text{-}o\text{-}C_6\mathit{H}_3\text{-}p\text{-}CH_3$	
and	6.7-8.5 m
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6\mathit{H}_5$	

$(\eta^5\text{-}C_5Me_4CH_2C_6H_4\text{-}m\text{-}CH_3)(\eta^5,\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}C_6H_4)Sc$ (18) [g]

$\eta^5\text{-}C_5(\mathit{CH}_3)_4CH_2C_6H_4\text{-}m\text{-}CH_3$	1.50 s
and	
$\eta^5,\eta^1\text{-}C_5(\mathit{CH}_3)_4CH_2\text{-}o\text{-}C_6H_4$	1.93 S
	1.99 s
	2.04 s
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6H_4\text{-}m\text{-}\mathit{CH}_3$	2.06 s
$\eta^5\text{-}C_5(CH_3)_4\mathit{CH}_2C_6H_4\text{-}m\text{-}CH_3$	4.09 br, s
$\eta^5,\eta^1\text{-}C_5(CH_3)_4\mathit{CH}_2\text{-}o\text{-}C_6H_4$	3.87 br, s
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6\mathit{H}_4\text{-}m\text{-}CH_3$	
and	6.7-8.5 m
$\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2\text{-}o\text{-}C_6\mathit{H}_4$	

$(\eta^5\text{-}C_5Me_4CH_2C_6H_4\text{-}m\text{-}CH_3)(\eta^5,\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CF_3)Sc$ (19) [g]

$\eta^5\text{-}C_5(\mathit{CH}_3)_4CH_2C_6H_4\text{-}m\text{-}CH_3$	1.39 s
and	
$\eta^5,\eta^1\text{-}C_5(\mathit{CH}_3)_4CH_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CF_3$	1.85 s
	1.94 s
	1.97 s
$\eta^5\text{-}C_5(CH_3)_4CH_2C_6H_4\text{-}m\text{-}\mathit{CH}_3$	2.06 s
$\eta^5,\eta^1\text{-}C_5(CH_3)_4\mathit{CH}_2\text{-}o\text{-}C_6H_3\text{-}p\text{-}CF_3$	3.78 br, s
$\eta^5\text{-}C_5(CH_3)_4\mathit{CH}_2C_6H_4\text{-}m\text{-}CH_3$	3.86 br, s

η^5-C$_5$(CH$_3$)$_4$CH$_2$C$_6$*H*$_4$-*m*-CH$_3$ and η^5,η^1-C$_5$(CH$_3$)$_4$CH$_2$-*o*-C$_6$*H*$_3$-*p*-CF$_3$	6.64-8.41 m

(η^5-C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-CF$_3$)(η^5,η^1-C$_5$Me$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-CH$_3$)Sc (20)[g]

η^5,η^1-C$_5$(C*H*$_3$)$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-CH$_3$	1.51 s
and	
η^5-C$_5$(C*H*$_3$)$_4$CH$_2$C$_6$H$_4$-*m*-CF$_3$	1.87 s
	1.93 s
	1.99 s
η^5,η^1-C$_5$(CH$_3$)$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-C*H*$_3$	2.38 s
η^5,η^1-C$_5$(CH$_3$)$_4$C*H*$_2$-*o*-C$_6$H$_3$-*p*-CH$_3$	3.83 br
η^5-C$_5$(CH$_3$)$_4$C*H*$_2$C$_6$H$_4$-*m*-CF$_3$	4.09 br
η^5,η^1-C$_5$(CH$_3$)$_4$CH$_2$-*o*-C$_6$*H*$_3$-*p*-CH$_3$ and η^5-C$_5$(CH$_3$)$_4$CH$_2$C$_6$*H*$_4$-*m*-CF$_3$	6.6-8.4 m

(η^5-C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-NMe$_2$)(η^5,η^1-C$_5$Me$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-CH$_3$)Sc (21)
and
(η^5-C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-CH$_3$)(η^5,η^1-C$_5$Me$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-NMe$_2$)Sc (22)[g]

	1.58 s
	1.61 s
η^5,η^1-C$_5$(C*H*$_3$)$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-CH$_3$	1.94 s
η^5,η^1-C$_5$(C*H*$_3$)$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-NMe$_2$	1.95 s
η^5-C$_5$(C*H*$_3$)$_4$CH$_2$C$_6$H$_4$-*m*-CH$_3$	2.01 s
η^5-C$_5$(C*H*$_3$)$_4$CH$_2$C$_6$H$_4$-*m*-NMe$_2$	2.05 s
	2.09 s
	2.16 s
η^5,η^1-C$_5$(CH$_3$)$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-N(C*H*$_3$)$_2$	2.75 s
η^5-C$_5$(CH$_3$)$_4$CH$_2$C$_6$H$_4$-*m*-N(C*H*$_3$)$_2$	2.47 s
η^5-C$_5$(CH$_3$)$_4$CH$_2$C$_6$H$_4$-*m*-C*H*$_3$	2.38 s
η^5,η^1-C$_5$(CH$_3$)$_4$CH$_2$-*o*-C$_6$H$_3$-*p*-C*H*$_3$	2.06 s
η^5-C$_5$(CH$_3$)$_4$C*H*$_2$C$_6$H$_4$-*m*-CH$_3$	3.84 s
η^5,η^1-C$_5$(CH$_3$)$_4$C*H*$_2$-*o*-C$_6$H$_3$-*p*-N(CH$_3$)$_2$	3.95 s
η^5,η^1-C$_5$(CH$_3$)$_4$C*H*$_2$-*o*-C$_6$H$_3$-*p*-CH$_3$	4.07 s
η^5-C$_5$(CH$_3$)$_4$C*H*$_2$C$_6$H$_4$-*m*-NMe$_2$	4.16 s
η^5,η^1-C$_5$(CH$_3$)$_4$CH$_2$-*o*-C$_6$*H*$_3$-*p*-N(CH$_3$)$_2$ η^5,η^1-C$_5$(CH$_3$)$_4$CH$_2$-*o*-C$_6$*H*$_3$-*p*-CH$_3$ η^5-C$_5$(CH$_3$)$_4$CH$_2$C$_6$*H*$_4$-*m*-NMe$_2$ η^5-C$_5$(CH$_3$)$_4$CH$_2$C$_6$*H*$_4$-*m*-CH$_3$	6.3–8.5 m

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[a] All ^{1}H NMR spectra were recorded in benzene–d_6 at 400 MHz unless otherwise noted. All signals are reference to internal tetramethylsilane unless otherwise noted.

[b] Coupling constants are reported in hertz.

[c] The ^{1}H NMR spectrum was recorded in THF–d_8 at 90 MHz.

[d] The ^{1}H NMR spectrum was recorded in CDCl$_3$ at 90 MHz.

[e] The ^{1}H NMR spectrum was recorded in benzene–d_6 at 90 MHz.

[f] The ^{1}H NMR spectrum was recorded in cyclohexane-d_{12} and referenced to the residual protio impurity.

[g] The ^1H NMR spectrum was recorded in benzene–d_6 at 500 MHz.

Note: The following abbreviations are used to denote the multiplicity of the NMR signals: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Experimental Section

General Considerations. All manipulations were performed using glovebox, high–vacuum[19] or Schlenk techniques. Solvents were purified by distillation from an appropriate drying agent under a N_2 atmosphere and either used immediately or vacuum–transferred from "titanocene" or sodium–benzophenone. Benzene–d_6 and cyclohexane–d_{12} were purified by vacuum transfer from activated molecular sieves (4 Å, Linde) and then from "titanocene". ^1H and ^{13}C NMR spectra were recorded on Varian EM–390 (90 MHz, ^1H), JEOL GX400Q (400 MHz, ^1H; 100 MHz, ^{13}C) and Brucker WM500 (500 MHz, ^1H) spectrometers. Elemental analyses were performed by Mr. Larry Henling of the CIT Analytical Laboratory.

Synthetic Procedures

Preparation of $Li^+(C_5(CH_3)_4CH_2C_6H_4$–*m*–$X)^-$ (X = H[20], CH_3, CF_3 and $N(CH_3)_2$).[21] Each ligand was prepared by the reaction of tetramethylcyclopentenone with the corresponding substituted benzyl Grignard reagent, followed by dehydration with *para*–toluene sulfonic acid when needed. In each case an excess of the substituted Grignard reagent (ca. 1.5 mol/mol of ketone) was allowed to react with tetramethylcyclopentenone. Due to the high boiling points of the ligands, purification and the final characterization was made by preparing the corresponding lithium salts.

(a) X = H; To 54 mmol of $BrMgCH_2C_6H_5$ in ca. 100 cm^3 of diethyl ether was added 36 mmol of tetramethylcyclopentenone. The reaction mixture was refluxed overnight, then quenched with ca. 30 cm^3 of H_20. The organic products were extracted into diethyl ether (2 X 50 cm^3). The ethereal extracts were concentrated to ca. 60 cm^3 and 0.5 g *para*–toluene sulfonic acid was added. The reaction mixture was stirred for 10 minutes at which time ca. 50 cm^3 of H_2O and 1 g of $NaHCO_3$ were added. The organic product was extracted with diethyl ether (2 X

50 cm^3), dried over Na_2SO_4 and concentrated under high vacuum to yield 7.1 g of yellow oil. To this 7.1 g of oil in ca. 100 cm^3 of diethyl ether (at –80 °C) was syringed 21 cm^3 of a 1.6 M n–butyllithium/hexane solution. After stirring for three hours at ambient temperatures a yellow precipitate had formed. This solid was collected by filtration, washed twice with diethyl ether and dried *in vacuo* to yield 4.2 g of $Li^+(C_5Me_4CH_2C_6H_5)^-$ (53% yield based on tetramethylcyclopentenone).

(b) X = CH_3; Following the procedure described above (for X = H), tetramethylcyclopentenone (5.0 g) and excess $BrMgCH_2C_6H_4$–*m*–CH_3 ultimately affords 4.4 g of $Li^+(C_5Me_4CH_2C_6H_4$–*m*–$CH_3)^-$ (52% based on tetramethylcyclopentenone). It should be noted that treatment of the initailly isolated organic product with *para*–toluene sulfonic acid is not necessary due to the alcohols spontaneous dehydration during work–up.

(c) X = CF_3; Again following the procedure described above (for X = H), tetramethylcyclopentenone (5.0 g) and excess $ClMgCH_2C_6H_4$–*m*–CF_3 ultimately affords 3.8 g of $Li^+(C_5Me_4CH_2C_6H_4$–*m*–$CF_3)^-$ (37% yield based on tetramethylcyclopentenone). The reaction time for the deprotonation of $HC_5Me_4CH_2C_6H_4$–*m*–CF_3 by *n*–butyllithium should be kept to a mimimum (ca. 1 hour). Longer reaction times result in a darkening of the reaction mixture and a reduced yield of the lithium salt.

(d) X = NMe_2; *M*eta–N,N–dimethylaminobenzyl potassium was prepared in N,N–dimethyl–*meta*–toluidine following previously described procedures[22]. *M*eta–N,N–dimethylaminobenzylmagnesium bromide was prepared by stirring the potassium salt with anhydrous $MgBr_2$ etherate in diethyl ether, followed by filtration to remove the KBr. To the filtrate was carefully added 5 g of tetramethylcyclopentenone and the resulting mixture was refluxed for 2 hours. The reaction was quenched with ca. 30 cm^3 of an aqueous solution containing 1 g of NaOH. The organic layer was separated and the aqueous layer was washed twice with 50 cm^3 portions of diethyl ether. The ether washings were combined and the volatiles were removed *in vacuo*. Residual

N,N–dimethyl–*meta*–toluidine was removed by gently heating (30–40 ° C) for 2–3 hours under hard vacuum. To the resulting alcohol was added 40 cm^3 of diethyl ether and 2.0 g of *para*–toluene sulfonic acid. After stirring approximately 15 minutes a water layer became evident. To this mixture an aqueous solution containing 2.0 g of NaOH was added, the organic phase was separated, and the aqueous solution was washed twice with 50 cm^3 portions of diethyl ether. The solvent was removed *in vacuo* to afford 5.1 g of viscous yellow oil. To the 5.1 of crude ligand in ca. 50 cm^3 of petroleum ether was added 12.5 cm^3 of n–butyllithium in hexane (1.6 M). The reaction was stirred for two hours, then filtered to collect the precipitate. The product was washed with petroleum ether and dried to afford 2.0 g (21 % based on tetramethylcyclopentenone) of pale yellow product.

Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)ScCl (1). (η^5–C_5Me_5)$ScCl_2$[14] (4.0 g, 15.9 mmol) and Li(η^5–$C_5Me_4CH_2CH_2CH_3$)[23] (3.0 g, 17.6 mmol) were heated in benzene at 110° C for three days. The solvent was removed *in vacuo* and the non–volatiles were washed into a flask with petroleum ether (40 cm^3) which was then attached to a frit assembly. The resultant suspension was filtered to remove the LiCl. Removal of the solvent *in vacuo* affords **1** as an amber oil in near quantitative yield (90–95 % pure by ^{1}H NMR).

Cp*(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)Sc (2). Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)ScCl (2.5 g, 6.6 mmol) and $LiCH_3$ (0.145 g, 6.6 mmol) were stirred for one hour in ca. 20 cm^3 of benzene. The suspension was filtered and the benzene was replaced with petroleum ether. Cooling to –78° C resulted in the precipitation of product which was collected as a pale yellow solid by filtration (0.9 g, 40%). Analysis: Found(calculated) %C 75.22 (74.13), %H 9.33 (9.33).

(η^5-$C_5Me_4CH_2C_6H_4$-*m*-CH_3)(η^5-$C_5Me_4CH_2CH_2CH_3$)ScCl (4). (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)$ScCl_2$ (0.64 g, 1.88 mmol) and excess Li(η^5–$C_5Me_4CH_2CH_2CH_3$) (0.42 g, 2.47 mmol) were refluxed overnight in ca. 25 *m*L of toluene. The solvent was replaced with petroleum ether and filtered to afford the product as an amber oil (essentially pure by ^{1}H NMR).

Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)$HfCl_2$ (6). (η^5–C_5Me_5)$HfCl_3$ (10.2 g, 24.3 mmol) and Li(η^5–$C_5Me_4CH_2CH_2CH_3$) (4.2 g, 24.7 mmol) were refluxed in xylenes for three days under an argon atmosphere. Removal of the xylene solvent (under reduced pressure) followed by an aqueous/methylene chloride work–up[24] gave 12.6 g (95%) of **6** as off–white crystals.

Cp*(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)HfH (8). A flask was charged with **6** (4.28 g, 7.8 mmol) and ca. 50 cm^3 of toluene. 10.7 cm^3 of a 1.6 M solution of n–butyllithium in hexane (2.2 equivalents of n–butyllithium) was added to the toluene suspension (at –78° C) under an argon flush. The argon was then replaced with one atmosphere of dihydrogen and the solution was allowed to warm with stirring. When the uptake of dihydrogen had ceased, the toluene was replaced with petroleum ether and the suspension was filtered. Removal of the petroleum ether *in vacuo* afforded an amber oil which consisted of an approximately equimolar ratio of Cp*(η^5–$C_5Me_4CH_2CH_2CH_3$)HfH_2 **(7)** and Cp*(η^5,η^1–$C_5Me_4CH_2CH_2CH_2$)HfH **(8)**. A benzene solution of this mixture was transfered to a small glass bomb which was heated to 80° for several hours, then evacuated to remove the generated dihydrogen. After three cycles the contents of the bomb were transfered to a frit assembly and the benzene was replaced with petroleum ether. Cooling to –78 °C and filtering afforded 1.8 g (50 %) of **8** as a colorless powder. Analysis: Found(calculated) %C 55.34 (55.43), %H 7.07 (7.13).

Cp*(η^5–$C_5Me_4CH_2C_6H_5$)$HfCl_2$ (9). (η^5–C_5Me_5)$HfCl_3$ (5.1 g, 12.1 mmol) and Li^+(η^5–$C_5Me_4CH_2C_6H_5$)$^-$ (2.7 g, 12.4 mmol) were refluxed in xylenes for three days under an argon atmosphere. Removal of the xylene solvent (under reduced pressure) followed by an aqueous/methylene chloride work–up gave 6.5 g (90%) of **9** as an off–white solid. Analysis: Found(calculated) %C 52.24(52.40), %H 5.53(5.75).

$Cp^*(\eta^5–C_5Me_4CH_2C_6H_5)Hf(CH_2C_6H_5)_2$. Approximately 20 cm^3 of benzene was condensed onto a mixture of **9** (1.94 g, 3.26 mmol) and excess benzylpotassium (1.39 g, 11.1 mmol). After stirring for 1 hour the suspension was filtered and the benzene was replaced with petroleum ether. Cooling to –78°C and filtering afforded 1.69 g (73%) of pale yellow $Cp^*(\eta^5–C_5Me_4CH_2C_6H_5)Hf(CH_2C_6H_5)_2$.

$Cp^*(\eta^5,\eta^1–C_5Me_4CH_2$–*o*–$C_6H_4)HfH$ (11). A large glass bomb was charged with 1.49 g (2.10 mmol) of $Cp^*(\eta^5–C_5Me_4CH_2C_6H_5)Hf(CH_2C_6H_5)_2$ and 25 cm^3 of toluene. The bomb was cooled to –196°C, evacuated, then refilled with one atmosphere of dihydrogen (ca. 4 atmospheres at 25°C). The solution was then stirred at 140°C for one day, recharged with dihydrogen, and stirred for a second day at 140°C. The ^1H NMR spectra of the crude reaction mixture showed the presence of $Cp^*(\eta^5–C_5Me_4CH_2C_6H_5)HfH_2$ **(10)** and $Cp^*(\eta^5,\eta^1–C_5Me_4CH_2$–*o*–$C_6H_4)HfH$ **(11)**. Three cycles of heating the mixture to 80°C followed by removal of the generated dihydrogen *in vacuo* produces colorless **11**, which was isolated in 79% yield (0.88 g) from –78°C petroleum ether. Analysis: Found(calculated) %C 59.39(59.48), %H 6.51(6.53).

$Cp^*(\eta^5–C_5Me_4CH_2C_6H_5)ScCl$. Cp^*ScCl_2 (1.4 g, 5.5 mmol) and $Li(\eta^5–C_5Me_4CH_2C_6H_5)$ (1.2 g, 5.5 mmol) were refluxed for 1 day in ca. 25 cm^3 toluene. Filtering the reaction mixture and removing the solvent *in vacuo* afforded $Cp^*(\eta^5–C_5Me_4CH_2C_6H_5)ScCl$ as an amber oil which was essentially pure by ^1H NMR.

$Cp^*(\eta^5,\eta^1–C_5Me_4CH_2$–*o*–$C_6H_4)Sc$ (12). $Cp^*(\eta^5–C_5Me_4CH_2C_6H_5)ScCl$ (1.97 g, 4.62 mmol) and methyllithium (100 mg, 4.55 mmol) were stirred for 3 hours in ca. 20 cm^3 of benzene. The benzene solvent was replaced with petroleum ether and the LiCl was removed by filtration. Cooling the solution to –78°C and filtering afforded 0.54 g (30% yield) of colorless **12**. Analysis: Found(calculated) %C 79.36 (79.97), %H 8.31 (8.52).

Generation of Cp*(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)Sc. Cp*$ScCl_2$ (90 mg, 0.36 mmol) and Li(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3) (83 mg, 0.36 mmol) were placed into a small glass bomb with 5 cm^3 of toluene and heated to 110°C for 1 day. To this reaction mixture was added $LiCH_2SiMe_3$ (34 mg, 0.36 mmol). After stirring overnight the toluene was removed *in vacuo* and the scandium product was extracted with benzene–d_6. This product, which was not isolated, exhibited a ^1H NMR spectrum consistent with Cp*(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)Sc.

(η^5–$C_5Me_4CH_2C_6H_4$–*meta*–X)Sc(acac)$_2$. (a) X = CH3; Sc(acac)$_3$ (15.0 g, 43.9 mmol) and Li(η^5–$C_5Me_4CH_2C_6H_4$–*meta*–CH_3) (11.2 g, 48.2 mmol) were refluxed in ca. 75 cm^3 of toluene for 12 hours. The toluene was removed *in vacuo* and the air–stable product was washed three times (3 X 50 cm^3) with anhydrous methyl alcohol to remove the $Li^+(acac)^-$. The product was dried *in vacuo* to yield 11.6 g (56%) of pale yellow (η^5–$C_5Me_4CH_2C_6H_4$–*meta*–CH_3)Sc(acac)$_2$.

(b) X = H; This air–stable compound was prepared in an analogous manner from 4.4 g of Sc(acac)$_3$ and 2.8 g of Li(η^5–$C_5Me_4CH_2C_6H_5$) to yield 4.1 g (71%) of product. Analysis: Found(calculated) %C 67.75(68.71), %H 7.18(7.32).

(η^5–$C_5Me_4CH_2C_6H_4$–*meta*–X)$ScCl_2$. (a) X = CH_3; (η^5–$C_5Me_4CH_2C_6H_4$–*meta*–CH_3)Sc(acac)$_2$ (11.6 g, 24.8 mmol) and $AlCl_3$ (6.61 g, 49.6 mmol) were stirred overnight in ca. 100 cm^3 of toluene. The resulting toluene suspension was heated to 100°C to dissolve the sparingly soluble products. Allowing the hot toluene solution to slowly cool to room temperature resulted in the precipitation of (η^5–$C_5Me_4CH_2C_6H_4$–*meta*–CH_3)$ScCl_2$, which was collected by filtration (5.2 g, 61%).

(b) X = H; This compound was prepared in an analogous manner from 4.14 g of (η^5–$C_5Me_4CH_2C_6H_5$)Sc(acac)$_2$ and 2.44 g of $AlCl_3$ to yield 2.2 g (74%) of (η^5–$C_5Me_4CH_2C_6H_5$)$ScCl_2$. Analysis: Found(calculated) %C 59.18(58.74), %H 6.00(5.85).

(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_5$)ScCl (14). (η^5–$C_5Me_4CH_2C_6H_5$)$ScCl_2$ (0.95 g, 2.9 mmol) and Li(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3) (0.67 g, 2.9 mmol) were refluxed overnight in ca. 15 cm^3 of toluene. Filtration, followed by removal of the solvent *in vacuo* yielded **14** as an amber oil which was essentially pure by ^{1}H NMR.

(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–X)ScCl (15, X = CF_3; 16, X = NMe_2).
(15) X = CF_3; (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)$ScCl_2$ (0.95 g, 2.79 mmol) and Li(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3) (0.80 g, 2.80 mmol) were refluxed for 3 hours in ca. 20 cm^3 of toluene. The toluene was replaced with petroleum ether and the solution was filtered. Cooling the petroleum ether solution to –78 °C and filtering afforded 0.77 g (47%) of **15** as an off–white powder.

(16) X = NMe_2; This compound was prepared in an analogous manner from 0.96 g (2.8 mmol) of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)$ScCl_2$ and 0.76 g (2.9 mmol) of Li(η^5–$C_5Me_4CH_2C_6H_4$–*m*–NMe_2) to yield 0.78 g (50%) of **16** as an off–white powder. Analysis: Found(calculated) %C 73.60(75.05), %H 7.59(8.10), %N 2.34(2.50).

Synthesis of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_4)Sc (18) and (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)(η^5–$C_5Me_4CH_2C_6H_5$)Sc (17) in a 2:1 ratio. Methyllithium powder (60 mg, 2.7 mmol) was added to a benzene solution of **14** (1.3 g, 2.5 mmol) and the reaction mixture was stirred for 2 hours. The benzene was replaced with petroleum ether and the solution was filtered. Cooling to –78 °C and filtering afforded **18** and **17** in a 2:1 mixture (0.65 g, 54%). Analysis: Found(calculated) %C 81.83 (82.47), %H 8.13 (8.18).

Synthesis of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CF_3)Sc (19) and (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)Sc (20) in a 1:1 (kinetic) ratio. Ca. 10 cm^3 of benzene was condensed onto a mixture of **15** (0.71 g, 1.21 mmol) and $LiCH_2SiMe_3$ (115 mg, 1.22 mmol) . After stirring for 1 hour the benzene was replaced with petroleum ether and the solution was filtered. Cooling the petroleum ether solution to −78 °C and filtering afforded 390 mg (59%) of the two isomers in approximately a 1:1 ratio (^{1}H NMR).

(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)ScC_6H_5. Approximately 20 cm^3 of benzene was condensed onto a mixture of **15** (0.92 g, 1.57 mmol) and phenyllithium (0.15 g, 1.79 mmol). This mixture was stirred for 1 hour at room temperature and filtered. The benzene was replaced with petroleum ether and cooled to −78 °C. Filtering afforded 0.53 g (54%) of the product as an off–white powder. Analysis: Found(calculated) %C 73.86 (76.66), %H 6.80(7.08).

Generation of 17 and 18 in a 16:1 (thermodynamic) ratio. Method a) Heating a sample of the 1:1 mixture of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CF_3)Sc and (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)Sc (isolated as desribed above) to 50 °C in benzene–d_6 shifts the ratio to 16:1 within 1/2 hour. This ratio was measured by integrating the benzyl methyl resonance of each isomer. Once established this ratio does not change, although decomposition is observed to slowly occur over the course of several hours. Method b) Heating benzene–d_6 solutions of (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–CF_3)ScC_6H_5 overnight at 50 °C cleanly generates benzene and a mixture of **17** and **18** in a 16:1 ratio. Samples generated in this manner do not undergo detectable decomposition until heated for several hours at 80 °C.

Generation of (η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–NMe_2)Sc (19) and (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5,η^1–$C_5Me_4CH_2$–*o*–C_6H_3–*p*–NMe_2)Sc (20) in a 1:1 ratio. Method a) Compound **14**, 22 mg, and C_6H_5Li, 4 mg, were sealed in an NMR tube with benzene–d_6. After *ca.* 15 minutes the ^{1}H NMR spectrum showed a single *species* identified as (η^5–$C_5Me_4CH_2C_6H_4$–*m*–CH_3)(η^5–$C_5Me_4CH_2C_6H_4$–*m*–NMe_2)ScC_6H_5. Heating

$(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}NMe_2)ScC_6H_5$ overnight at 50 °C resulted in the generation of C_6H_6 and a 1:1 mixture of **19** and **20**. Heating this sample to 80 °C did not alter this ratio.

Method b). $(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}CH_3)(\eta^5\text{–}C_5Me_4CH_2C_6H_4\text{–}m\text{–}NMe_2)ScC_6H_5$ was generated as described above in a NMR tube attached to a Kontes needle valve. A catalytic amount of dihydrogen (*ca.* 20 torr) was admitted to the tube which was then sealed with a torch. Heating the tube overnight at 50 °C resulted in the generation of C_6H_6 and a 1:1 mixture of **19** and **20**.

Measurement of Equilibrium Constants. The equilibration of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)HfH$ **(8)** and dihydrogen with $Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)HfH_2$ **(7)** (equation 13) was studied in the following manner. Compound **8** (16.8 mg, 0.034 mmol) was placed in a sealable NMR tube along with 0.481 g of benzene–*d*$_6$ and the tube was attached to a Kontes teflon–stoppered valve. The solvent was cooled to –78 °C and the tube was evacuated. The benzene–*d*$_6$ was kept frozen at –78 °C, but the remainder of the tube was allowed to warm to room temperature. Dihydrogen (282 torr) was admitted to the tube which was then sealed with a torch. The volume of space above the frozen benzene–*d*$_6$ was measured, allowing for the initial amount of dihydrogen in the NMR tube to be calculated. Subsequent equilibrations were carried out in a constant temperature ethylene glycol bath which was judged to be constant to ± 0.2 °C. The equation describing the equilibrium constant is given below.

$$K_{eq} = \frac{[H_2]\,[\mathbf{8}]}{[\mathbf{7}]}$$

The concentrations of **8** and **7** were determined from the relative heights of the resonances at δ 1.92 and 2.05, respectively. The total amount of dihydrogen in the NMR tube is given by equation 22.

$$\text{total mmol } H_2 = (\text{mmol } H_2)_{\text{initial}} - \text{mmol } Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)HfH_2 \qquad (22)$$

A knowledge of the total amount of dihydrogen in the NMR tube allowed for the concentration of dihydrogen in solution to be calculated as desribed elsewhere[7]. In order to obtain a unitless equilibrium constant the concentration of each species was expressed as a mole fraction. The equilibrium constants for equation 3 and 16 were determined in an analogous manner.

The equilibration of $Cp^*(\eta^5\text{–}C_5Me_4CH_2CH_2CH_3)Sc\text{–}C_6H_5$ (**3**) with benzene and **2** (equation 8) was studied by sealing 29 mg (0.085 mmol) of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2CH_2CH_2)Sc$ **(2)** in a NMR tube along with 56 mg of C_6H_6 (0.72 mmol) and 0.487 g of cylohexane–d_{12}. The equation describing the equilibrium constant is given by:

$$K_{eq} = \frac{[C_6H_6]\,[\mathbf{2}]}{[\mathbf{3}]}$$

The concentrations of **2** and **3** were determined from the relative heights of their respective Cp* resonances. The total amount of C_6H_6 in the NMR tube is expressed by equation 23.

$$\text{total mmol } C_6H_6 = (\text{mmol } C_6H_6)_{\text{initial}} - \text{mmol } \mathbf{3} \qquad (23)$$

The amount of dissolved C_6H_6 was calculated at each temperature using Henry's law. Concentrations were expressed as mole fractions in order to obtain unitless equilibrium constants.

A lower limit for the (Sc–alkynyl) BDE relative to the (Sc-aryl) BDE was established in the following manner. *Tert*–butylacetylene (0.016 mmol) was condensed into an NMR tube which contained 0.033 mmol of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2\text{–}o\text{–}C_6H_4)Sc$,**12**, and 0.65 g of benzene–d_6 and the tube was sealed. The ^1H NMR spectrum revealed a 1 to 1 mixture of 12 and a species identified as $Cp^*(\eta^5\text{–}C_5Me_4CH_2C_6H_5)Sc\text{–}C{\equiv}CCMe_3$,**13**; there was no evidence for unreacted *tert*–butylacetylene. Assuming as much as 2% *tert*–butylacetylene could be presence yet undetected by ^1H NMR, lower values for K_{eq} and $\Delta G°$ in equation 19 are $1.4 \times 10^2\ M^{-1}$ and $-3\ kcal \cdot mol^{-1}$, respectively. If a value for $\Delta S°$ of -15 e.u. is assumed, $\Delta H° \leq 7.5\ kcal \cdot mol^{-1}$, and since $H\text{–}C{\equiv}CCMe_3$ BDE = 132(5) $kcal \cdot mol^{-1}$**[13]** and $H\text{–}C_6H_5$ BDE = 111 $kcal \cdot mol^{-1}$**[13]**, the (Sc–alkynyl) BDE must be ≥ 29(5) $kcal \cdot mol^{-1}$ stronger than the (Sc–aryl) BDE.

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(2) Caution should be exercised in concluding too much from this type of reactivity, however, since these reaction could, in large part, be due to the very strong thermodynamic driving force. Moreover, coordination of the Bronsted acid to the metal center prior to deprotonation is likely in many cases.

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(7) The validity of this statement depends on (*i*) the H–C_6H_5 and (η^5–$C_5Me_4CH_2C_6H_4$–*o*–*H*) BDEs being equal and (*ii*) the Hf–aryl BDE not depending on the orientation of the phenyl ring relative to the hafnocene equatorial plane. The possibility also exists that these two effects may cancel, at least in part.

(8) ^{1}H NMR integration was carried out at 50 °C.

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(16) A roughly linear correlation is found for BDE(H–R) *vs.* BDE(Sc–R) (R = alkynyl, aryl, alkyl), with a slope of 0.8, not the unity value of the Bryndza/Bercaw correlation. Similar, less-than-unity slopes have been noted by others for transition metal–hydrocarbyl bonds: see reference 12(d) and the contribution by Bergman and co-workers in *Polyhedron*, in press.

(17) So far as we are aware, no substituent effects on the M–aryl (M = alkali or alkaline earth metal) BDE's have been examined. Thus, these results suffer from the lack of a point of reference.

(18) Steigerwald, M. L.; Goddard, W. A. *J. Am. Chem. Soc.*, **1984**, *106*, 308.

(19) Burger, B. J.; Bercaw, J. E. in "New Developments in the Synthesis, Manipulation and Characterization of Organometallic Compounds", *ACS Symposium Series,* A. Wayda and M. Darensbourg, Eds., in press.

(20) An alternative synthesis of $C_5Me_4(CH_2C_6H_5)H$ has been published: Blaha, J.P.; Wrighton, M.S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

(21) We have found that the *meta*–methoxide derivative $Li^+(\eta^5–C_5Me_4CH_2C_6H_4–m–OMe)^-$ can also be prepared by methods analogous to those described here.

(22) Schlosser, M.; and Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

(23) Threlkel, R. S. and Bercaw, J. E. *J. Organomet. Chem.*, **1977**, *136,* 1.

(24) Wolczanski, P. T., Bercaw, J. E. *Organometallics*, **1982**, *1*, 793.

Chapter V

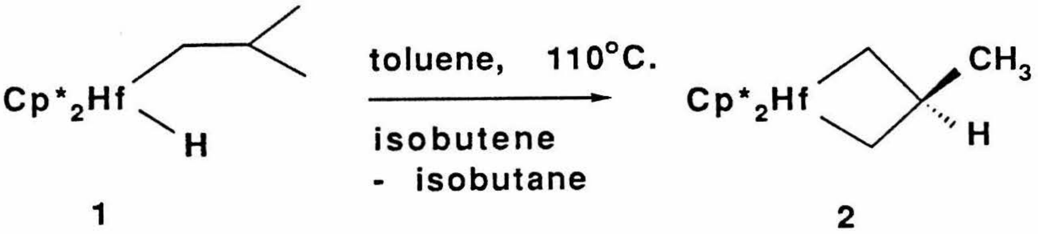
The Mechanism of Dihydrogen Elimination from Hydrido Alkyl Derivatives of Permethylhafnocene. The Molecular Structure of $Cp^*_2\overline{HfCH_2CH(CH_3)C}H_2$.

Introduction

There are numerous examples of transition metal complexes, although often of limited stability, which contain cis–alkyl and hydride ligands. Complexes of this type are frequently observed as the products of arene or alkane C–H bond activation at low valent transition metal centers. The reverse process of oxidative addition, reductive elimination, is a common mode of decomposition for cis–hydrido alkyl or aryl complexes, particularly for the later transition metals.[1] Studies of the thermal decomposition of early transition metal complexes containing cis hydride and alkyl ligands are rare, a notable exception being the elimination of isobutane from $Cp^*_2Zr(CH_2CHMe_2)H$ to form pentamethylcyclopentadienyl metallated zirconium species.[2] In contrast, the thermolysis of benzene–d_6 solutions of $Cp^*_2Hf(CH_2CHMe_2)H$ has been shown to result in dihydrogen elimination concurrent with the formation of $Cp^*_2\overline{HfCH_2CHMeC}H_2$.[3] Intrigued by this latter observation, we have undertaken an investigation into the mechanism of dihydrogen loss from $Cp^*_2Hf(CH_2CHMe_2)H$ (and from complexes of the type $Cp^*_2Hf(R)H$ in general), the results of which are reported herein.

Results and Discussion

As previously shown by Roddick and Bercaw, heating benzene–d_6 solutions of the isobutyl hydride complex $Cp^*_2Hf(CH_2CHMe_2)H$ (**1**) results in the formation of a 1:1 mixture of $Cp^*_2HfH_2$ and the β substituted metallacyclobutane $Cp^*_2\overline{HfCH_2CHMeC}H_2$ (**2**) plus 1/2 equivalent of isobutane.[3] In the presence of excess isobutene metallacycle **2** is formed quantitatively (equation 1).



(1)

In order to confirm the structure of the hafnium metallacycle **2**, the crystal structure has been determined by X–ray diffraction techniques.

The molecular structure of **2** is presented in Figure 1 and the atomic labeling is given in Figure 2. As can be seen from the figures, the metallacyclic ring of **2** adopts a puckered conformation in the solid state with the β carbon being displaced 0.384 Å out of the plane formed by Hf, C12 and C13. This distortion from planarity may serve to minimize an unfavorable steric interaction between one of the Cp* rings and the β–methyl substituent of the hafnacyclobutane ring. In contrast, titanacyclobutanes of the type $Cp_2TiCH_2CH(R)CH_2$, which are active olefin metathesis catalysts (unlike **2**), have been found to have essentially planar metallacyclic rings.[4]

The formation of **2** has been proposed to occur by the concerted loss of dihydrogen from **1** via a simple four–centered transition state at the Hf(IV) (Figure 3).[3]

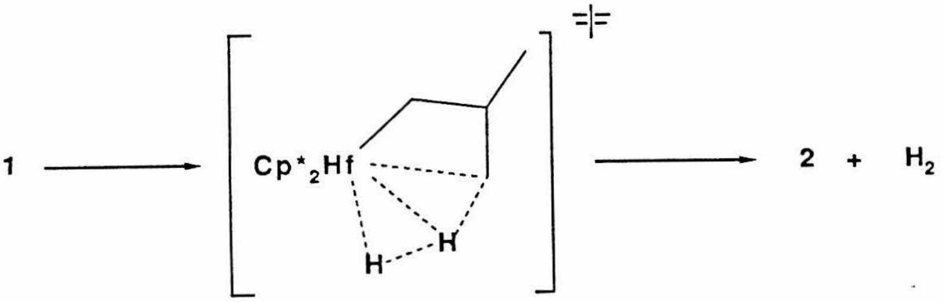


Figure 3. The proposed transition state for the conversion of **1** to **2** and dihydrogen.

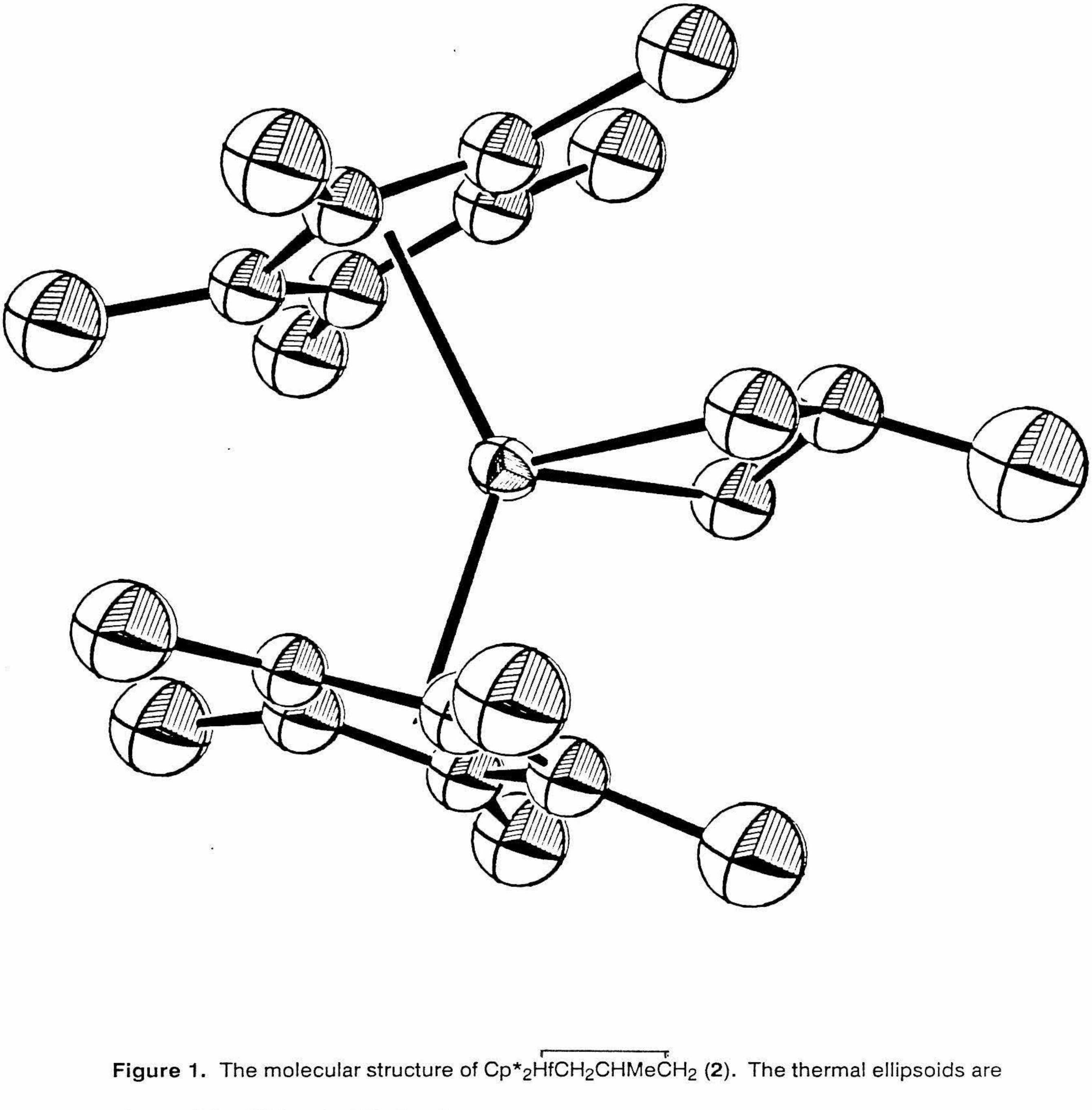


Figure 1. The molecular structure of $\mathrm{Cp^*{}_2\overline{HfCH_2CHMeCH_2}}$ (**2**). The thermal ellipsoids are shown at the 50% probability level.

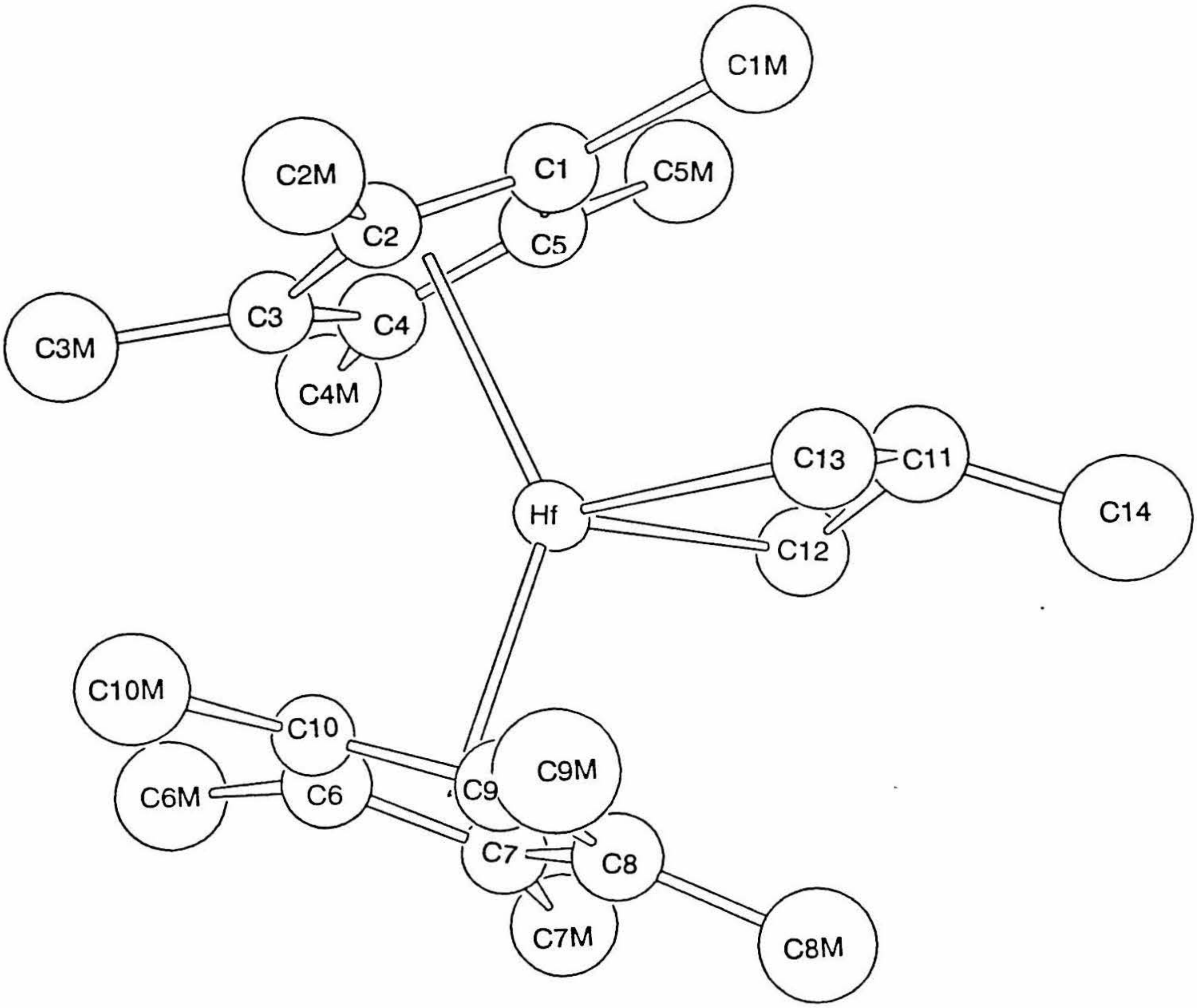


Figure 2. The atomic labeling for $Cp^*_2\overline{HfCH_2CH(CH_3)C}H_2$ (**2**).

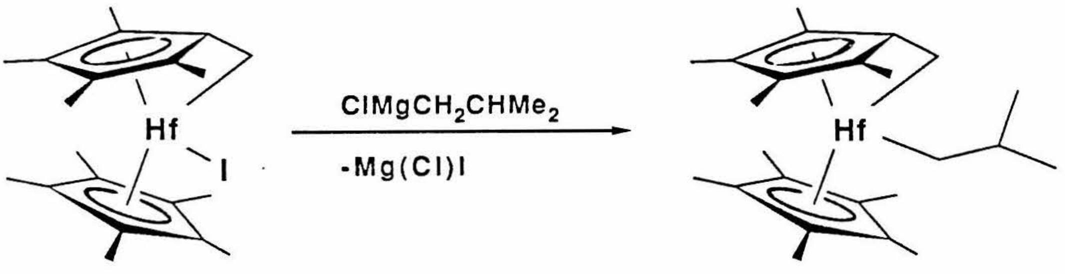
Table 1. Complete Bond Distances and Angles for $Cp^*_2\overline{HfCH_2CH(CH_3)CH_2}$ (**2**).

Atom	Atom	Dist. (Å)	Atom	Atom	Atom	Angle
Hf	C1	2.563(10)	R1	Hf	R2	138.4
Hf	C2	2.509(10)	C12	Hf	C13	70.2(4)
Hf	C3	2.524(9)	C5	C1	C2	109.1(9)
Hf	C4	2.502(9)	C1M	C1	C2	126.8(9)
Hf	C5	2.539(10)	C1M	C1	C5	123.8(9)
Hf	C6	2.529(7)	C3	C2	C1	107.8(8)
Hf	C7	2.558(9)	C2M	C2	C1	124.8(9)
Hf	C8	2.582(9)	C2M	C2	C3	127.1(9)
Hf	C9	2.558(9)	C4	C3	C2	108.4(8)
Hf	C10	2.532(9)	C3M	C3	C2	125.5(9)
Hf	C12	2.249(10)	C3M	C3	C4	124.3(9)
Hf	C13	2.238(11)	C5	C4	C3	108.2(8)
C11	C12	1.522((15)	C4M	C4	C3	126.4(9)
C11	C13	1.581(16)	C4M	C4	C5	125.0(9)
C11	C14	1.530(20)	C4	C5	C1	106.3(8)
Hf	R1	2.225	C5M	C5	C1	125.8(8)
Hf	R2	2.251	C5M	C5	C4	127.7(8)
C1	C2	1.382(14)	C10	C6	C7	105.7(7)
C1	C5	1.434(14)	C6M	C6	C7	123.8(8)
C1	C1M	1.529(17)	C6M	C6	C10	128.8(8)
C2	C3	1.404(13)	C8	C7	C6	109.1(8)
C2	C2M	1.493(16)	C7M	C7	C6	123.3(9)
C3	C4	1.409(12)	C7M	C7	C8	127.5(9)
C3	C3M	1.504(16)	C9	C8	C7	107.6(8)
C4	C5	1.411(13)	C8M	C8	C7	125.5(9)
C4	C4M	1.497(16)	C8M	C8	C9	126.4(9)
C5	C5M	1.778(14)	C10	C9	C8	108.7(8)
C6	C7	1.430(11)	C9M	C9	C8	124.6(9)
C6	C10	1.433(12)	C9M	C9	C10	126.4(9)
C6	C6M	1.469(14)	C9	C10	C6	109.0(8)
C7	C8	1.403(13)	C10M	C10	C6	126.8(9)
C7	C7M	1.512(17)	C10M	C10	C9	123.1(9)
C8	C9	1.414(13)	C13	C11	C12	112.5(9)
C8	C8M	1.516(17)	C14	C11	C12	112.2(11)
C9	C10	1.389(13)	C14	C11	C13	112.4(11)
C9	C9M	1.500(15)				
C10	C10M	1.489(17)				

R1 and R2 are the centroids of the C1 through C5 and the C6 through C10 rings, respectively.

Such a mechanism is consistent with the observation that the rate of conversion of **1** to **2** is independent of the concentration of added isobutene and that no intermediates are observed when the reaction is followed by ^{1}H NMR.[3] Thus, a mechanism involving the rate–determining insertion of isobutene into the Hf–H bond of **1** to form $Cp^*_2Hf(CH_2CHMe_2)_2$, followed by the rapid loss of isobutane through a four–centered transition state, is considered unlikely. These observations, however, do not eliminate mechanisms involving *(i)* metallated pentamethylcyclopentadienyl intermediates or *(ii)* pentamethylcyclopentadiene intermediates derived from the migration of the hydride ligand to a (η^5–C_5Me_5) ring.

A mechanism involving the metallated pentamethylcyclopentadienyl derivative $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2CH(CH_3)_2$ is deserving of consideration (recall that the conversion of $Cp^*_2Hf(CH_2C_6H_5)_2$ to $Cp^*_2HfCH_2\text{–}o\text{–}C_6H_4$ and toluene proceeds through the metallated benzyl derivative $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2C_6H_5$[5]). Thus, $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfCH_2CH(CH_3)_2$ (**3**) was prepared from the metallated iodide complex $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ (**4**) (equation 2).[5]



(2)

4 **3**

Thermolysis of **3** in the presence of >10 equivalents of added isobutene results in a complex mixture of products including *ca.* 30% of **2**. This contrasts with the essentially quantitative conversion of the isobutyl hydride to complex **2**. Thus, a mechanism involving the intermediacy of $Cp^*(\eta^5,\eta^1\text{--}C_5Me_4CH_2)HfCH_2CH(CH_3)_2$ is deemed unlikely.

The presence of β hydrogens in **1** precludes deuterium labeling studies of the hydride ligand of **2**. While samples of $Cp^*_2Hf(CH_2CDMe_2)D$ can be prepared from $Cp^*_2HfD_2$ and isobutene, H/D exchange between the Cp* ligands and the deuteride position occurs upon thermolysis (presumably *via* $Cp^*_2HfD_2$, although $Cp^*_2Hf(CH_2CDMe_2)D$ is the only species observed by ^1H NMR) and consequently makes the desired labeling study impossible. We therefore turned our attention to hydrido alkyl complexes of permethylhafnocene which lack β hydrogens.

The method used to prepare hydrido alkyl derivatives of permethylhafnocene which lack β–hydrogens is shown below (equations 3–5).

$$Cp^*_2HfI_2 + LiCH_2CMe_3 \longrightarrow Cp^*_2Hf(CH_2CMe_3)I + LiI \qquad (3)$$

$$Cp^*_2Hf(CH_2CMe_3)I + H_2 \longrightarrow Cp^*_2Hf(H)I + CMe_4 \qquad (4)$$

$$Cp^*_2Hf(H)I + M'R \longrightarrow Cp^*_2Hf(H)R + M'I \qquad (5)$$

5; $R = CH_2C_6H_5$
6; $R = C_6H_4\text{–}o\text{–}CH_3$
M' = Li or K

These syntheses take advantage of the facile hydrogenation of $Cp^*_2Hf(CH_2CMe_3)I$ to yield $Cp^*_2Hf(H)I$ and neopentane. Treating $Cp^*_2Hf(CH_2CMe_3)I$ with D_2 cleanly affords

$\mathrm{Cp^*_2Hf(D)I}$. Subsequent treatment of $\mathrm{Cp^*_2Hf(H)I}$ with alkyl potassium reagents affords the corresponding hydrido–alkyl complexes **5** and **6**.

Mild thermolysis of benzene–d_6 solutions of **5** affords an equimolar mixture of $\mathrm{Cp^*_2HfH_2}$ and the hafnabenzometallacyclobutene derivative $\mathrm{Cp^*_2}\overline{\mathrm{HfCH_2{-}o{-}C}}\mathrm{{}_6H_4}$ (**7**) plus one half of an equivalent of toluene (equation 6).

$$\underset{\mathbf{5}}{2\,\mathrm{Cp^*_2Hf(CH_2C_6H_5)H}} \longrightarrow \underset{\mathbf{7}}{\mathrm{Cp^*_2}\overline{\mathrm{HfCH_2{-}}\mathit{o}\mathrm{{-}C}}\mathrm{{}_6H_4}} + \mathrm{Cp^*_2HfH_2} + \mathrm{C_6H_5CH_3} \qquad (6)$$

Traces of the ortho–tolyl hydride complex **6** are also observed in the final product mixture (the final concentration of **6** amounts to ≤10% of **7** or $\mathrm{Cp^*_2HfH_2}$ as determined by ^{1}H NMR). The decomposition of **5** follows first order kinetics for ≥ 2 half lifes. Construction of an Arrhenius plot from the rate data given in Table 2 yields the activation parameters $\Delta H^\ddagger$ = 25.6(5) kcal·mol^{-1} and $\Delta S^\ddagger$ = −8(2) e.u..

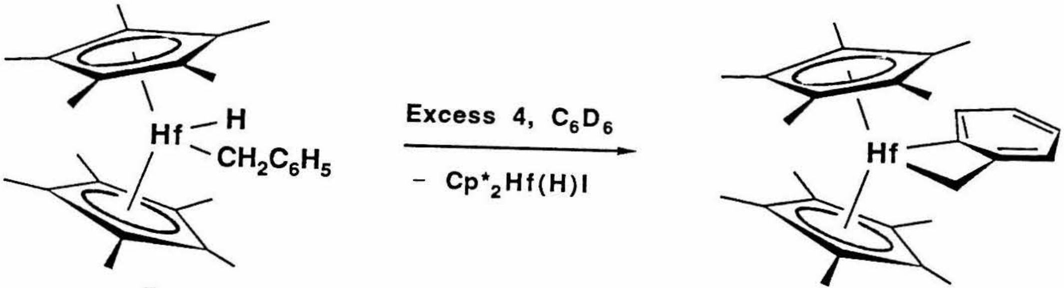
Table 2. Rate Constants for the Thermal Decomposition of $\mathrm{Cp^*_2Hf(CH_2C_6H_5)H}$ (**5**).

Temperature (°C)	k(x 10^{-6} sec^{-1})^a	k(x 10^{-6} sec^{-1})^b
46	1.1(1)	
62	7.7(2)	4.2(1)
70.5	20(1)	

$\Delta H^\ddagger$ = 25.6(5)kcal mol^{-1}
$\Delta S^\ddagger$ = −8(2) e.u.^{c}

[a] These rate data were obtained in benzene–d_6 solvent in the absence of **4**. The organometallic products of the reaction were **7** and $\mathrm{Cp^*_2HfH_2}$.
[b] This rate constant was obtained in benzene–d_6 solvent in the presence of *ca.* 10 equivalents of **4**. The organometallic products of the thermolysis were **7** and $\mathrm{Cp^*_2Hf(H)I}$.
[c] For the purpose of constructing an Arrhenius plot the rate constants obtained in the absence of **4** were halved and therefore reflect the actual rate of dihydrogen loss from **5**.

If the thermolysis of **5** is carried out in the presence of a large excess of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ **4**, first order kinetics are again observed, but with a rate constant which is approximately half that observed in the absence of **4** (Table 2). Neither toluene nor $Cp^*_2HfH_2$ is detected, rather equimolar amounts of metallacycle **7** and hydrido iodide **1** are the final products (equation 7).



5 **7** (7)

These results are consistent with the initial formation of **7** and dihydrogen upon thermolysis of **5**. In the absence of an effective H_2 trap, such as **4**[6], the dihydrogen reacts with another equivalent of **5** to generate $Cp^*_2HfH_2$ and toluene. As the reaction proceeds and the relative concentration of **7** increases, the hydrogenation of **7** to give $Cp^*_2Hf(C_6H_4\text{–}o\text{–}CH_3)H$,**6**, becomes competitive with the hydrogenation of **5**.[7] In the presence of *ca.* 10 equivalents of **4**, however, the formed dihydrogen preferentially reacts with **4** to give $Cp^*_2Hf(H)I$, and **5** decomposes at a rate which is half that observed in the absence of **4**.

In an order to probe the mechanism by which dihydrogen is lost from **5**, the isotopically labeled benzyl hydride derivatives $Cp^*_2Hf(CH_2C_6H_5)H$ **5a**, $Cp^*_2Hf(CD_2C_6D_5)H$ **5b**, $Cp^*_2Hf(CH_2C_6H_5)D$ **5c**, $Cp^*_2Hf(CD_2C_6H_5)H$ **5d**, $Cp^*_2Hf(CD_2C_6D_5)D$ **5e**, and $(Cp^*\text{–}d_{15})_2Hf(CH_2C_6H_5)H$ **5f** were prepared (equation 8).

$$(\eta^5\text{–}C_5(CW)_5)_2Hf(X)I + KCY_2C_6Z_5 \xrightarrow[-\,KI]{\text{benzene}} (\eta^5\text{–}C_5(CW)_5)_2HfCY_2C_6Z_5(X) \tag{8}$$

5a; W=X=Y=Z=H
5b; W=X=H, Y=Z=D
5c; W=Y=Z=H, X=D
5d; W=X=Z=H, Y=D
5e; W=H, X=Y=Z=D
5f; W=D, X=Y=Z=H

As can be seen from Table 3, deuteration of the benzyl methylene group (**5d**) has no effect on the rate of decomposition of **5** (k_H/k_D = 1.1(1) at 62°C), thus precluding an α–H abstraction process as a significant pathway. This is in contrast to $Cp^*{}_2Hf(CH_2C_6H_5)_2$, which has been shown to decompose predominately by an α–H abstraction mechanism forming an unstable hafnium benzylidene species and toluene.[5] Similarly, deuteration of the pentamethylcyclopentadienyl ligands (**5f**) has little effect on the rate of decomposition (k_H/k_D = 0.95(5) at 62°C). This result eliminates a rate limiting coupling of a ring methyl hydrogen with the hydride or the benzyl ligand as a likely mechanism, that is, the rate limiting formation of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)Hf(CH_2C_6H_5)$ is not operative in the decomposition of **5**. Furthermore, deuterium is not scrambled into the hydride position during the thermolysis (62°C) of **5f** eliminating a pre–equilibrium between $(Cp^*\text{–}d_{15})_2Hf(CH_2C_6H_5)H$ and $(Cp^*\text{–}d_{15})(\eta^5,\eta^1\text{–}C_5(CD_3)_4CD_2)Hf(CH_2C_6H_5)$ and HD followed by rate determining transfer of an ortho–benzyl hydrogen to the cyclopentadienyl methylene group as a significant pathway. A substantial kinetic isotope effect is observed upon deuteration of the benzyl ligand (**5b**) (k_H/k_D = 5.9(4) at 62°C), consistent with an ortho–benzyl C–D bond cleavage in the rate determining step. Interestingly, deuteration of the hydride ligand (**5c**) results in an inverse isotope effect upon pyrolysis (k_H/k_D = 0.78(3) at 62°C). Likewise, an inverse isotope effect is observed when the decomposition of **5e** (both the benzyl and hydride ligands are deuterated) is compared to that of **5b** (only the benzyl ligand is deuterated) (k_H/k_D = 0.57(5) at 62°C, Figure 4).

Table 3. Rate constants for the thermal decomposition of deuterium labeled **5** at 62 °C in the presence of excess Cp*(η^5,η^1-$C_5Me_4CH_2$)HfI.[a]

Compound	k(x 10^{-6} sec^{-1})	K_H/K_D
5	4.21(7)	———
5b	0.71(3)	5.9
5c	5.39(1)	0.78(3)
5d	3.94(14)	1.1(1)
5e	1.25(4)	3.4(5)
5f	4.42(7)[b]	0.95(5)

[a] These thermolyses were carried out in benzene-d_6.

[b] This value was obtained in the absence of Cp*(η^5,η^1-$C_5Me_4CH_2$)HfI. Hence, the value listed is half the observed rate of decomposition.

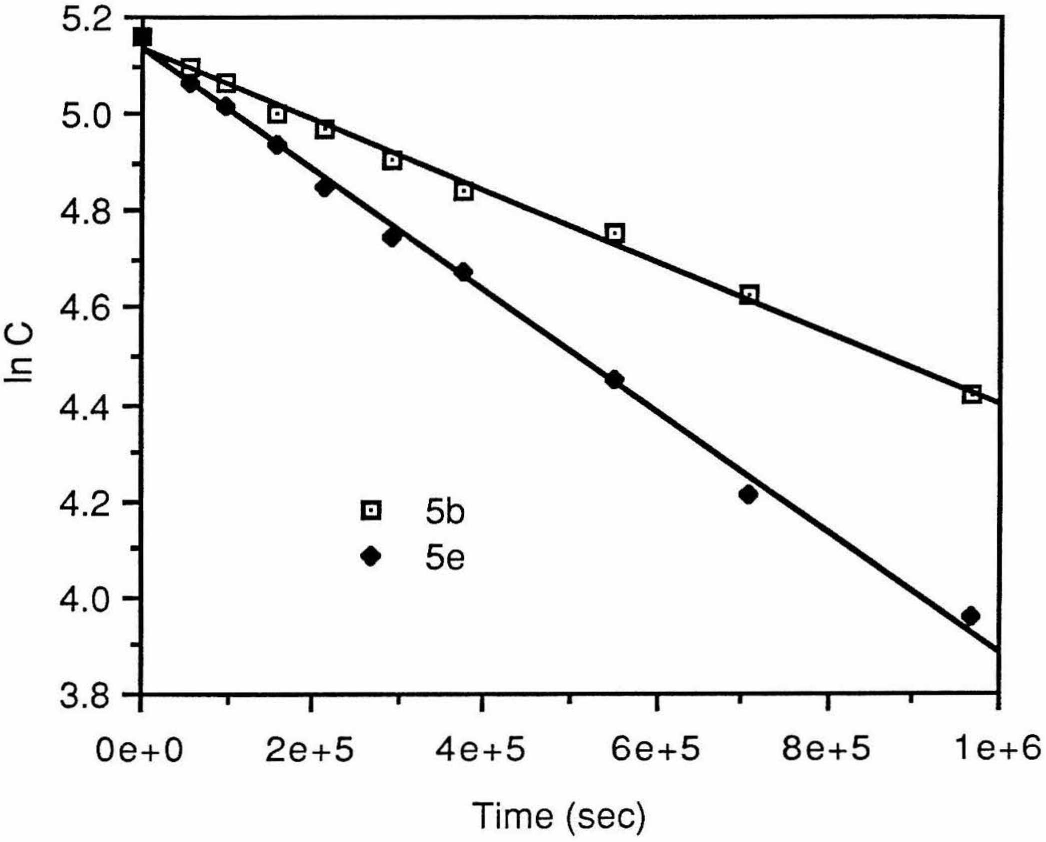
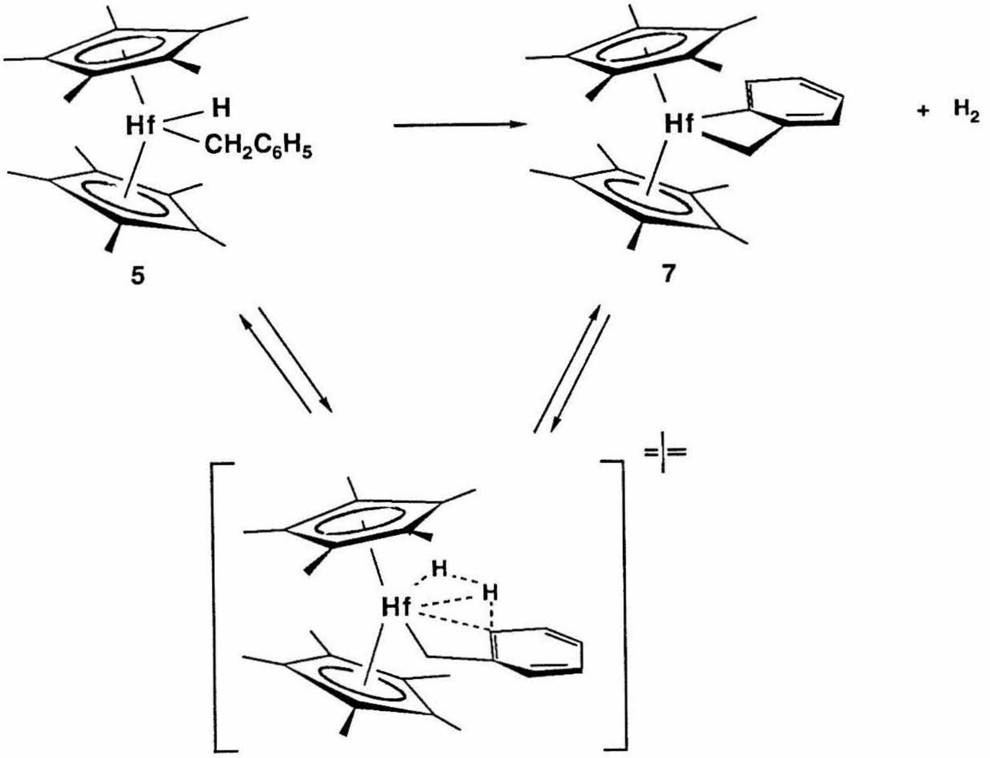


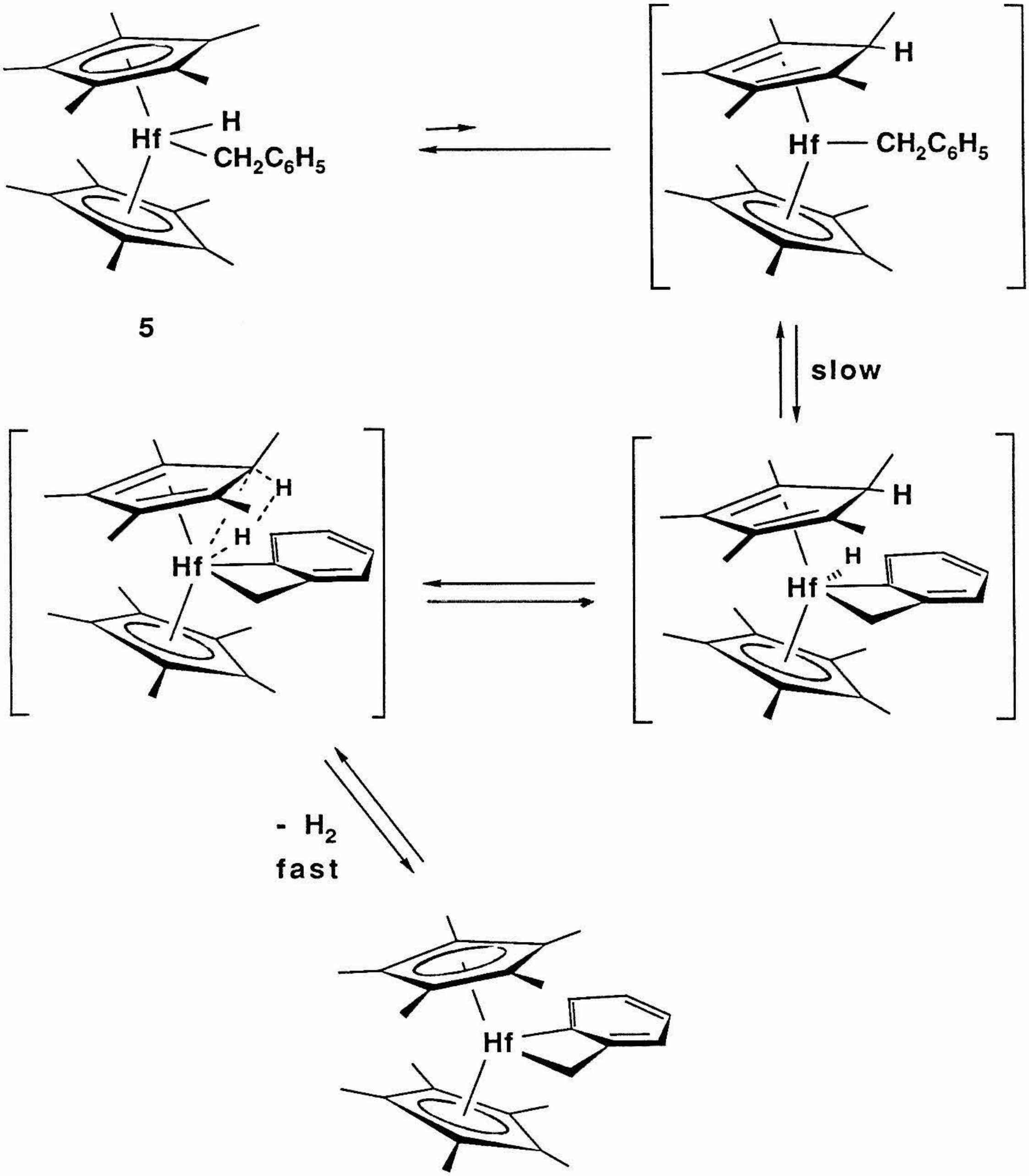
Figure 4. First order plots of the decomposition of $Cp^*_2Hf(CD_2C_6D_5)D$ (**5e**) and $Cp^*_2Hf(CD_2C_6D_5)H$ (**5b**) (K_H/K_D = 0.57(5) at 62 °C).

Two alternative mechanisms consistent with the rate determining cleavage of an ortho–benzyl C–H bond are depicted in Schemes 1 and 2. The mechanism shown in Scheme 1 involves the concerted loss of dihydrogen via a simple four–centered transition state at the Hf(IV) center.



Scheme 1. A potential mechanism for the formation of **7** and dihydrogen from **5**.

Although this mechanism is consistent with the rate determining cleavage of an ortho–benzyl carbon–hydrogen bond, it does not offer a straightforward explanation for the inverse kinetic isotope effect observed upon deuteration of the hydride ligand. In theory, an inverse deuterium isotope effect for a single, very endothermic, elementary step can occur if that step involves the transfer of hydrogen from a relatively low frequency

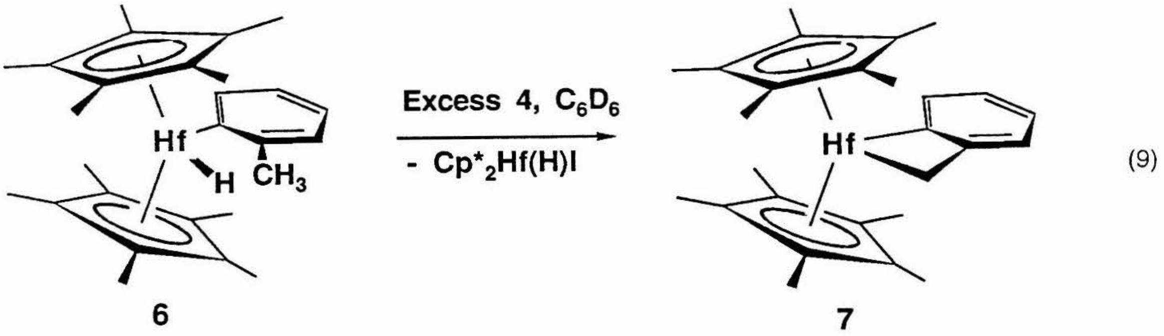


Scheme 2. An alternative mechanism for the formation of **7** and dihydrogen from **5**.

oscillator to a much higher frequency oscillator.[8] While the hydride is indeed being transferred to a higher frequency oscillator (a H–*H* bond is being formed at the expense of a Hf–*H* bond), the available evidence suggests that the overall reaction is to a first approximation, thermoneutral. This evidence is provided from thermochemical data[9] which indicate that the Hf–aryl bond dissociation energy (BDE) of **5** and the Hf–H BDE of **2** are approximately equal. Using the literature value of 104 kcal·mol^{-1} for the H–H BDE[10] and a value of 110 kcal·mol^{-1} for the ortho–benzyl BDE[11], and assuming a $\Delta S°$ of +15 e.u. for the transformation of **5** to **7** and dihydrogen[12] (which makes the loss of H_2 *ca.* 5 kcal·mol^{-1} more favorable at 62 °C), we can estimate that the overall free energy change is small. It should be noted that this estimate neglects any ring strain in the metallacyclic product which would serve to make the reaction more endothermic.

The rapid reversible migration of the hydride ligand to the pentamethylcyclopentadienyl ring proposed in Scheme 2 is followed by the rate limiting oxidative addition of an ortho–benzyl C–H bond to the Hf(II) center[13], and the final rapid elimination of dihydrogen to afford **7**. This mechanism is consistent with the normal primary isotope effect observed for **5b** (as was the mechanism depicted in Scheme 1). The mechanism presented in Scheme 2 is also consistent with the inverse isotope effects observed when the hydride ligand is deuterated, that is, the deuterium prefers to reside on the higher frequency oscillator (C–D rather than Hf–D). Although rare, intramolecular migrations of hydride and alkyl ligands to cyclopentadienyl rings have been directly observed.[14,15] Such migrations have, on several other occasions, been inferred.[16] Brintzinger has proposed that the hydrogenation of $Cp^*_2Zr(CH_2CMe_3)X$ proceeds by the initial attack of dihydrogen on the cyclopentadienyl–zirconium σ–bond (through a transition state analogous to that proposed in Scheme 2 for the final elimination of dihydrogen), followed by the transfer of the endo cyclopentadiene hydrogen to the neopentyl group.[17]

Pyrolysis of benzene–d_6 solutions of $Cp^*_2Hf(C_6H_4\text{–}o\text{–}CH_3)H$ **6** in presence of **4** cleanly affords a 1:1 ratio of metallacycle **7** and $Cp^*_2Hf(H)I$ (equation 9). The disapppearence of **6** follows first order kinetics when thermolysed in the presence of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ (Table 4). In the absence of **4**, the themolysis of **6** results in the formation of **7** with lesser amounts of $Cp^*_2HfH_2$ as well as uncharacterized decomposition products. It is interesting to note that the activation parameters for the conversion of **6** to **7** and dihydrogen ($\Delta H^‡$ = 24.0(5) kcal·mol^{-1} and $\Delta S^‡$ = −11(2) e.u.) are very similar to those obtained for the conversion of **5** to **7** and dihydrogen (see Tables 2 and 4). As with **5**, an



6 **7** (9)

Table 4. Rate Constants for the Thermal Decomposition of **6** in the presence of excess $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ (in benzene–d_6).

Temperature (°C)	k(x 10^{-6} sec^{-1})	K_H/K_D
51	1.82(2)	
64.5	8.39(30)	
80	42.3(14)	
80	49.8(12)[a]	0.85(4)
$\Delta H^‡$ = 24.0(5) kcal mol^{-1}		
$\Delta S^‡$ = −11(2) e.u.		

[a] The rate of decomposition of $Cp^*_2Hf(C_6H_4\text{–}o\text{–}CH_3)D$ in the presence of $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$.

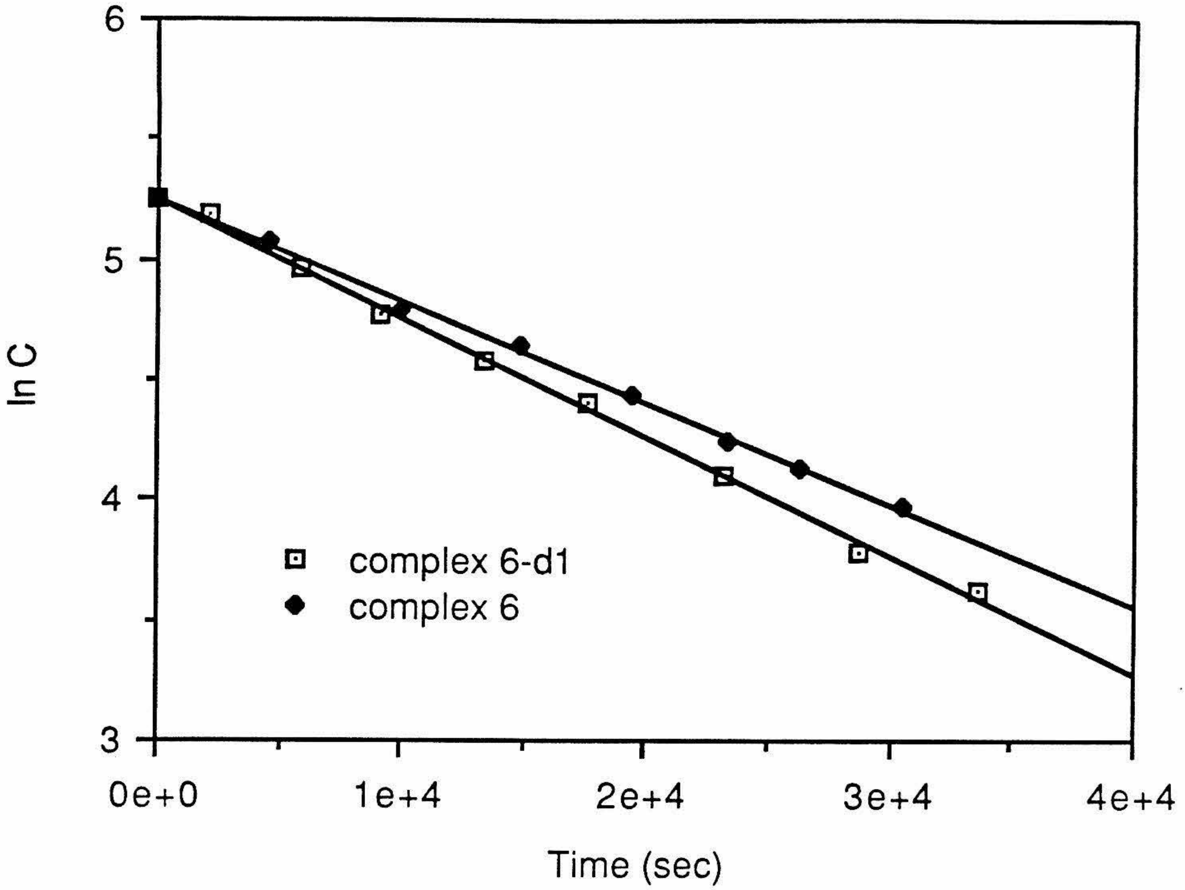


Figure 4. First order plots of the rate of decomposition of Cp*$_2$Hf(C_6H_4–*o*–CH_3)H (**6**) and Cp*$_2$Hf(C_6H_4–*o*–CH_3)D (**6**–*d_1*) (K_H/K_D = 0.85(4) at 80°C).

inverse isotope effect is observed when the hydride ligand of **6** is replaced by deuterium (k_H/k_D = 0.85(4), Figure 4). Based on this inverse isotope effect, a mechanism analogous to Scheme 2 is tentatively proposed, that is, a rapid pre–equilibrium is established with the hydride migrating between hafnium and the Cp* ligand, followed by the rate limiting addition of a tolyl methyl C–H bond to the 14e^- hafnium center. The rapid elimination of dihydrogen affords **7**. It must be emphasized that the evidence for this mechanism is limited to a single inverse isotope effect; however, the suggested mechanism does allow one to envision a common decomposition pathway for various Cp*$_2$Hf(R)H derivatives.

Conclusions

In summary, it has been demonstrated that thermolysis of benzene–d_6 solutions of the permethylhafnocene alkyl hydride complexes **1**, 5, and **6** results in the elimination of dihydrogen and the formation of new hafnium–containing species. In no case does decomposition proceed by the coupling of the hydride ligand with the adjacent alkyl substituent, nor does the coupling of ring methyl hydrogens with the alkyl substituent seem to be operative. For **1** the initially formed complex is $Cp^*_2HfCH_2CHMeCH_2$ (**2**), which has been crystallographically characterized. For both **5** and **6** the initially formed complex is $Cp^*_2\overline{HfCH_2\text{–}o\text{–}C}_6H_4$. Kinetic isotope effects of the decomposition of $Cp^*_2Hf(CH_2C_6H_5)H$ (**5**), are consistent with the rate limiting step cleavage of the ortho–benzyl C–H bond. Interestingly, an inverse isotope effect is found when the hydride ligands of **5** and **6** are deuterated, consistent with a rapid pre–equilibrium involving the transfer of the hydride ligand to the Cp* ring, followed by the rate limiting cleavage of an ortho–benzyl C–H bond (Scheme 2). Unfortunately, we are unable to test for an analogous inverse isotope effect for reaction 1 due to the facility with which the hydride position of $Cp^*_2Hf(CH_2CHMe_2)H$ (**1**) exchanges with the Cp* hydrogens.

Table 5. ^{1}H NMR data[a].

Compound	Assignment	δ (ppm)	Coupling[b]
Cp*(η^5,η^1–$C_5Me_4CH_2$)Hf(CH_2CHMe_2) (3)			
	$C_5(CH_3)_5$	1.90	
	$C_5(CH_3)_4CH_2$	1.57	
		1.73	
		1.89	
		2.07	
	$C_5(CH_3)_4CH_2$		
	$CH_2CH(CH_3)_2$	0.77 d	$^3J_{HH} = 9$
		1.13 d	$^3J_{HH} = 9$
	$CH_2CH(CH_3)_2$	*not observed*	
	$CH_2CH(CH_3)_2$	1.45 d	$^2J_{HH} = 7$
		1.92 d	$^2J_{HH} = 7$
Cp*$_2$Hf(H)I	$C_5(CH_3)_5$	2.03	
	Hf–*H*	15.3	
Cp*$_2$Hf($CH_2C_6H_5$)H (5)	$C_5(CH_3)_5$	1.90	
	$CH_2C_6H_5$	1.17	
	$CH_2C_6H_5$	6.8–7.2 m	
	Hf–*H*	13.6	
Cp*$_2$Hf(C_6H_4–*o*–CH_3)H (6)	$C_5(CH_3)_5$	1.85	
	C_6H_4–*o*–CH_3	2.15	
	C_6H_4–*o*–CH_3	6.02 m	
		7.0 m	
	Hf–*H*	14.0	

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[a] Spectra were recorded in benzene–d_6 and are referenced to internal tetramethylsilane.
[b] Coupling constants are given in hertz.

Experimental

General Considerations. All manipulations were performed using glovebox, high–vacuum[18] or Schlenk techniques. Solvents were purified by distillation from an appropriate drying agent under a N_2 atmosphere and either used immediately or vacuum–transferred from "titanocene" or sodium–benzophenone. Benzene–d_6 was purified by vacuum transfer from activated molecular sieves (4 Å, Linde) and then from "titanocene". ^{1}H NMR spectra were measured on Varian EM–390 (90 MHz, ^{1}H NMR) and JEOL GX400Q (400 MHz, ^{1}H NMR) spectrometers. Elemental analyses were performed by Mr. L. Henling of the CIT analytical department.

Synthetic Procedures:

$Cp^*_2Hf(D)I$. $Cp^*_2Hf(CH_2CMe_3)I$ (1.13 g, 1.7 mmol) was placed in a large glass bomb (with a volume of approximately 400 mL) with *ca.* 20 mL of benzene. Deuterium gas (one atmosphere) was admitted into the bomb at –196 °C. This solution was stirred at room temperature for 2 days (Note: heating results in incorporation of deuterium into the Cp* rings). The contents of the bomb were transferred to a frit assembly and the product (0.46 g, 47%) was isolated from –78 °C petroleum ether.

$Cp^*_2Hf(H)I$. This complex is prepared as described for $Cp^*_2Hf(D)I$ and can be isolated in *ca.* 50% yield. The reaction time can be reduced to 1 day if the hydrogenation is carried out at 80° C.

$Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)Hf(CH_2CH(CH_3)_2)$ (3). $Cp^*(\eta^5,\eta^1\text{–}C_5Me_4CH_2)HfI$ (0.66 g, 1.15 mmol) and 1.2 mmol $ClMg(CH_2CH(CH_3)_2)$ in diethyl ether were stirred in benzene for 1 hour. The solvent was replaced with petroleum ether. Filtering and cooling to –78 °C affords 288 mg of pale orange **3**. Elemental analysis: Found(calculated) %C 55.44 (57.08), %H 7.38 (7.58).

$Cp^*_2Hf(CH_2C_6H_5)H$ (5). $Cp^*_2Hf(H)I$ (0.50 g, 0.87 mmol) was stirred 1 hour with benzylpotassium (0.14 g, 1.04 mmol) in ca. 20 mL of benzene. The solution was filtered and the solvent was replaced with petroleum ether. Cooling the solution to –78 °C and filtering affords **2** as an off–white powder (0.20 g, 43%). The deuterated analogs **5b–5f** were prepared similarly from $Cp^*_2Hf(H)I$ and the appropriate benzylpotassium reagent.

$Cp^*_2Hf(C_6H_4$–*o*–$CH_3)H$ (6). $Cp^*_2Hf(H)I$ (785 mg, 1.36 mmol) and an excess of LiC_6H_4–*o*–CH_3 (250 mg, 2.55 mmol) were stirred overnight in benzene, then filtered to remove the LiCl. The product (0.30 g, 41%) was isolated from –78 °C petroleum ether. Elemental analysis: Found(calculated) %C 59.36 (59.93), %H 6.86 (7.08).

Kinetic Measurements of Thermal Decomposition. With the exception of the decomposition of **5f**, all reactions were followed by monitoring the decrease in height of the pentamethylcyclopentadienyl resonance of starting complex relative to internal $(\eta^5\text{–}C_5H_5)_2Fe$. The rate of decomposition of **5f** was followed by monitoring the decrease in integrated intensity of the $(Cp^*\text{–}d_{15})_2Hf(CH_2C_6H_5)H$ signal relative to $(\eta^5\text{–}C_5H_5)_2Fe$. NMR spectra were recorded at timed intervals using a Varian EM–390 (90 MHz) spectrometer. Reaction temperatures were maintained using constant temperature oil baths controlled by thermoregulators and were observed to be constant to within ±1°C. A typical experiment involved 25 mgs of hafnium complex and 6–10 mg of ferrocene dissolved in 0.4 mL of benzene–d_6. The NMR tubes were sealed containing >1 atm of dinitrogen. Peak heights were demonstrated to be reproducible to within ±7% by repeated measurement. Each spectrum was recorded 3 times and the average peak height was used to calculate the values of k given in Tables 2–4. Errors in k represent approximately 1 standard deviation.

Plots of ln(k/T) vs. 1/T were constructed from the decomposition rates and yielded the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

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(6) The addition of dihydrogen to a benzene–d_6 solution of Cp*(η^5,η^1–$C_5Me_4CH_2$)HfI immediately generates Cp*$_2$Hf(H)I. See Chapter II of this thesis.

(7) In a separate experiment, benzene–d_6 solutions of **7** were shown to react with dihydrogen (ca. 4 atmospheres) to initially afford **6**, which is subsequently hydrogenated to toluene and Cp*$_2$HfH$_2$. No Cp*$_2$Hf($CH_2C_6H_5$)H (**5**) is detected by ^{1}H NMR.

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