Normal and Inverse Primary Kinetic Deuterium Isotope Effects for C−H Bond Reductive Elimination and Oxidative Addition Reactions of Molybdenocene and Tungstenocene Complexes: Evidence for Benzene σ-Complex Intermediates

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Abstract: The overall reductive elimination of RH from the *ansa*-molybdenocene and -tungstenocene complexes [Me$_2$Si(C$_5$Me$_4$)$_2$]Mo(Ph)H and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(R)H (R = Me, Ph) is characterized by an inverse primary kinetic isotope effect (KIE) for the tungsten system but a normal KIE for the molybdenum system. Oxidative addition of PhH to {[Me$_2$Si(C$_5$Me$_4$)$_2$]M} also differs for the two systems, with the molybdenum system exhibiting a substantial intermolecular KIE, while no effect is observed for the tungsten system. These differences in KIEs indicate a significant difference in the reactivity of the hydrocarbon adducts [Me$_2$Si(C$_5$Me$_4$)$_2$]M(RH) for the molybdenum and tungsten systems. Specifically, oxidative cleavage of [Me$_2$Si-(C$_5$Me$_4$)$_2$]M(RH) is favored over RH dissociation for the tungsten system, whereas RH dissociation is favored for the molybdenum system. A kinetics analysis of the interconversion of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H, accompanied by elimination of methane, provides evidence that the reductive coupling step in this system is characterized by a normal KIE. This observation demonstrates that the inverse KIE for overall reductive elimination is a result of an inverse *equilibrium* isotope effect (EIE) and is not a result of an inverse KIE for a single step. A previous report of an inverse kinetic isotope effect of 0.76 for C−H reductive coupling in the [Tp]Pt(CH$_3$)H$_2$ system is shown to be erroneous. Finally, a computational study provides evidence that the reductive coupling of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H proceeds via the initial formation of a benzene σ-complex, rather than an η^2-π-benzene complex.

Introduction

The oxidative addition and reductive elimination of C−H bonds at a transition metal center are reactions that are of fundamental relevance to the functionalization of hydrocarbons.[1] An important discovery for this class of reaction was that hydrocarbon σ-complexes [M](σ-HR), i.e. complexes in which the hydrocarbon is coordinated to the metal by three-center, two-electron M···H−C interactions,[2] play an important role as key intermediates.[3,4] Evidence for the existence of these σ-complexes

comes from many sources. In addition to low-temperature spectroscopic and room-temperature flash kinetics studies,[3,5] the principal evidence for σ-complex intermediates is derived from the use of isotopic labeling experiments: specifically, (i) the observation of deuterium exchange between hydride and alkyl sites, e.g. [M](CH$_3$)D → [M](CH$_2$D)H, and (ii) the measurement of kinetic isotope effects (KIEs).[6] In this paper, we report a series of kinetic and thermodynamic deuterium isotope effects pertaining to the reactions of *ansa*-molybdenocene and -tungstenocene complexes of the type [Me$_2$Si(C$_5$Me$_4$)$_2$]M(R)H (M = Mo, R = Ph; M = W, R = Me, Ph). This study demonstrates that the KIEs are highly dependent on the nature of the metal, thereby indicating that the energy surface for reductive elimination of RH varies significantly for two otherwise similar systems.

Results and Discussion

(1) Synthesis of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Me)H and [Me$_2$Si-(C$_5$Me$_4$)$_2$]W(Ph)H. We are presently interested in defining how a [Me$_2$Si] *ansa* bridge modulates the reactivity of permethylated metallocene complexes by comparing the chemistry of Cp*$_2$-

(1) For recent reviews, see: (a) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437−2450. (b) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley and Sons: New York, 1989. (c) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. (d) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424. (e) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91−100. (f) Special issue: *J. Organomet. Chem.* **1996**, *504* (1−2). (g) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932. (h) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514.
(2) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537−1550, and ref 28 therein.
(3) (a) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125−3146. (b) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987−1007. (c) Crabtree, R. H. *Angew. Chem., Int. Edit. Engl.* **1993**, *32*, 789−805. (d) *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory, and Reactivity*; Kubas, G. J., Ed.; Kluwer Academic/Plenum Publishers: New York, 2001.
(4) Although hydrocarbon σ-complexes were originally formulated for an interaction of a transition metal with a single C−H bond, it has been noted that other coordination modes are possible, involving the simultaneous interaction with two or three C−H bonds. In this paper we use the term [M](σ-HR) to refer generally to σ-complexes without specifying the exact coordination mode, since this is often unknown.

(5) For a recent example of a σ-complex that has been characterized by NMR spectroscopy, see: Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953−9954.
(6) For recent reviews, see: (a) Jones, W. D. *Acc. Chem. Res.*, in press. (b) Bullock, R. M.; Bender, B. R. Isotope Methods in Homogeneous Catalysis. In *Encyclopedia of Catalysis*; Horváth, I. T., Ed.; Wiley: New York, 2003.

Scheme 1
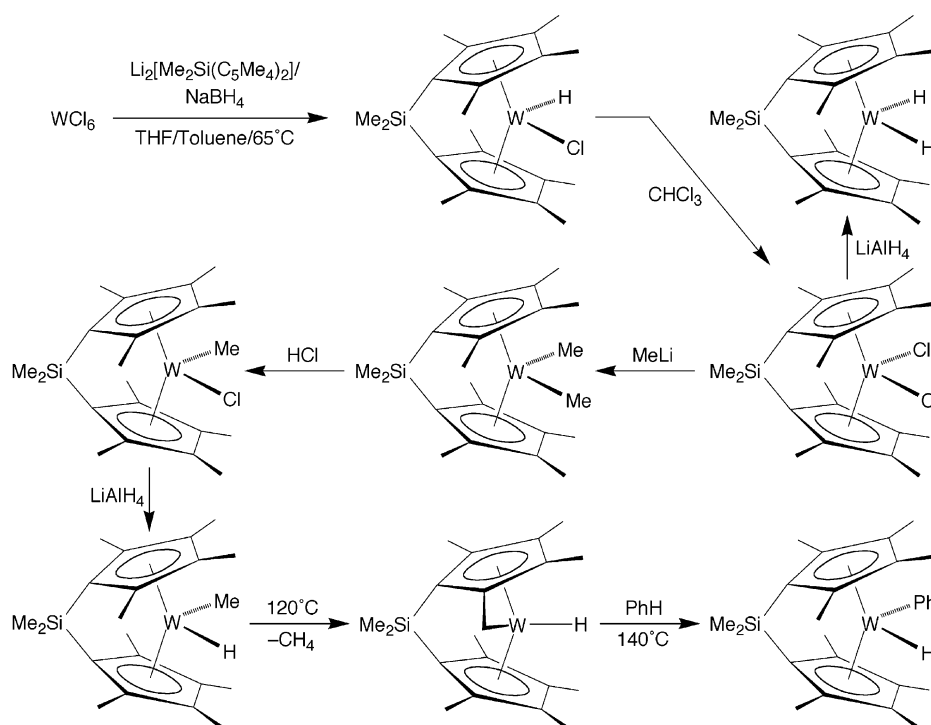
Scheme 2
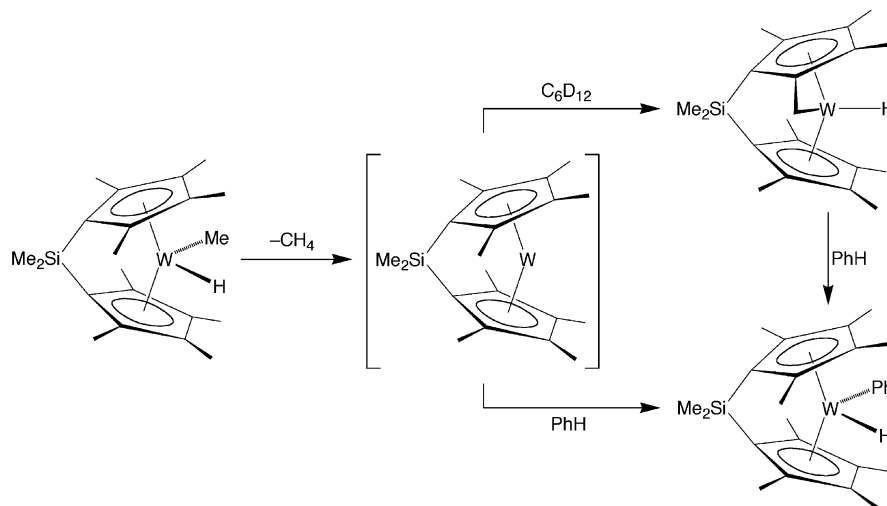
MX_n and $[Me_2Si(C_5Me_4)_2]MX_n$ systems.[7] As part of the course of these studies, we desired to investigate the influence of a [Me_2Si] *ansa* bridge on the reductive elimination of RH from complexes of the type $[Me_2Si(C_5Me_4)_2]M(R)H$ (M = Mo, W) and thereby obtain more insight into the mechanism of this fundamental reaction. While the molybdenum phenyl hydride complex $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ has previously been synthesized by photolysis of $[Me_2Si(C_5Me_4)_2]MoH_2$ in benzene,[7b] the tungsten complexes $[Me_2Si(C_5Me_4)_2]W(Me)H$ and $[Me_2Si(C_5Me_4)_2]W(Ph)H$ were previously unknown. Access to these

complexes is, nevertheless, provided by the sequence illustrated in Scheme 1. The molecular structures of $[Me_2Si(C_5Me_4)_2]WH_2$, $[Me_2Si(C_5Me_4)_2]WCl_2$, $[Me_2Si(C_5Me_4)_2]WMe_2$, and $[Me_2Si(C_5Me_4)_2]W(Ph)H$, as determined by X-ray diffraction, are illustrated in Figure 1.

(2) Reductive Elimination of Methane from [Me₂Si-(C₅Me₄)₂]W(Me)H: Intra- and Intermolecular C−H Bond Cleavage Reactions. Previous studies have demonstrated that the methyl hydride complex $Cp*_2W(Me)H$ undergoes reductive elimination of methane to give the tuck-in complex $Cp*(\eta^6\text{-}C_5Me_4CH_2)WH$ as a result of intramolecular trapping of the tungstenocene intermediate $[Cp*_2W]$.[8] The *ansa*-bridged complex $[Me_2Si(C_5Me_4)_2]W(Me)H$ likewise reductively eliminates methane in cyclohexane to give $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^6\text{-}C_5Me_3\text{-}CH_2)]WH$ (Scheme 2). In view of the fact that elimination of methane from $[Me_2Si(C_5Me_4)_2]W(Me)H$ yields the tuck-in

(7) See, for example: (a) Churchill, D. G.; Bridgewater, B. M.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 178−179. (b) Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. *Organometallics* **1999**, *18*, 2403−2406. (c) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255−3256. (d) Shin, J. H.; Parkin, G. *Chem. Commun.* **1999**, 887−888. (e) Lee, H.; Bonanno, J. B.; Hascall, T.; Cordaro, J.; Hahn, J. M.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1365−1368. (f) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.

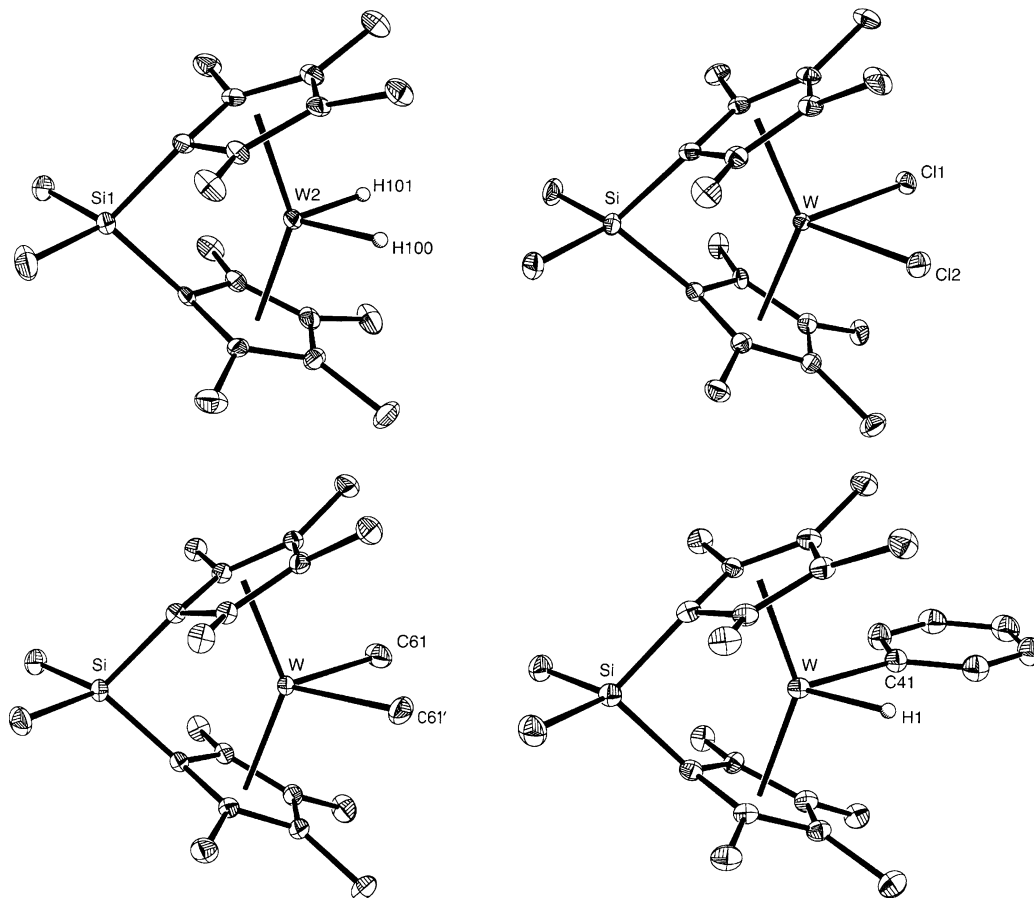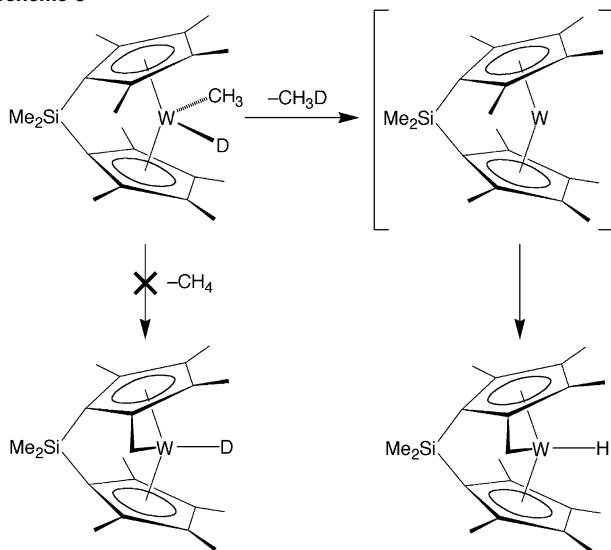(8) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172−1179.

Figure 1. Molecular structures of [Me$_2$Si(C$_5$Me$_4$)$_2$]WH$_2$, [Me$_2$Si(C$_5$Me$_4$)$_2$]WCl$_2$, [Me$_2$Si(C$_5$Me$_4$)$_2$]WMe$_2$, and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H.

Scheme 3

Table 1. Rate Constant and Activation Parameters for Reductive Elimination of Methane from [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Me)H in C$_6$D$_6$

T/°C	k_{obs}/s^{-1}	T/°C	k_{obs}/s^{-1}
100	3.74(5) × 10^{-6} [a]	140	1.35(3) × 10^{-4}
121	4.93(7) × 10^{-5}	159	7.95(16) × 10^{-4}
$\Delta H^{\ddagger} = 27.3(2.6)$ kcal mol^{-1}; $\Delta S^{\ddagger} = 10(6)$ e.u.			

[a] $k_{Cp^*} = 1.13(6) \times 10^{-4}$ s^{-1} for Cp*$_2$W(Me)H (Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172−1179).

(CD$_3$)D gives [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WH. These experiments support a reductive elimination mechanism for [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Me)H, in accord with that proposed for Cp*$_2$W(Me)H.[8]

Although the reductive elimination of methane from Cp*$_2$W(Me)H and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Me)H bear similarities, there are several interesting differences between the two systems. First, the *ansa* bridge substantially inhibits the reductive elimination of methane, with $k_{ansa}/k_{Cp^*} = 0.03$ at 100 °C (Table 1).[9] This inhibitory effect of the [Me$_2$Si] bridge is noteworthy in the sense that the same bridge actually promotes reductive elimination in the related tantalum system.[7d]

A second interesting difference between the two systems is observed using benzene as solvent. Thus, whereas reductive elimination of methane from Cp*$_2$W(Me)H gives only the tuck-

complex [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WH, consideration needs to be given to the possibility that the transformation involves an alternative mechanism involving the direct abstraction of a ring methyl hydrogen. However, decisive evidence that the reaction does indeed involve initial reductive elimination is provided by deuterium labeling studies. Specifically, thermolysis of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D liberates CH$_3$D and forms [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WH, rather than giving CH$_4$ and [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WD (Scheme 3). Likewise, elimination of methane from [Me$_2$Si(C$_5$Me$_4$)$_2$]W-

(9) Green has reported an even more dramatic effect, with [Me$_2$C(C$_5$H$_4$)$_2$]W-(Me)H being stable to elimination of methane under the conditions studied. See: (a) Labella, L.; Chernega, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 395−402. (b) Chernega, A.; Cook, J.; Green, M. L. H.; Labella, L.; Simpson, S. J.; Souter, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225−3243.
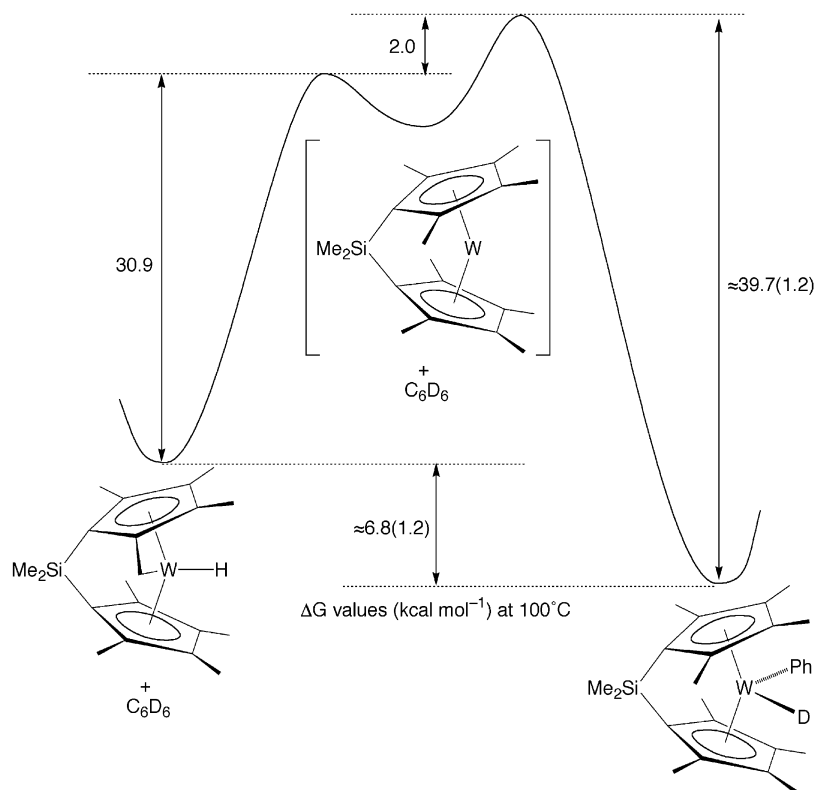
Figure 2. Free energy surface relating the products of intramolecular and intermolecular benzene C−H bond activation by {[Me$_2$Si(C$_5$Me$_4$)$_2$]W} at 100 °C, illustrating that intramolecular C−H bond activation is kinetically favored, but that the [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WH product is thermodynamically unstable with respect to conversion to [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H. $\Delta G^\ddagger$ for reductive elimination of C$_6$D$_6$ at 100 °C is estimated from the value at 182 °C, assuming that $\Delta S^\ddagger$ is in the range +15 to −15 e.u. The value of 6.8 kcal mol^{-1} for ΔG was not measured directly but is obtained via a thermodynamic cycle.

Scheme 4
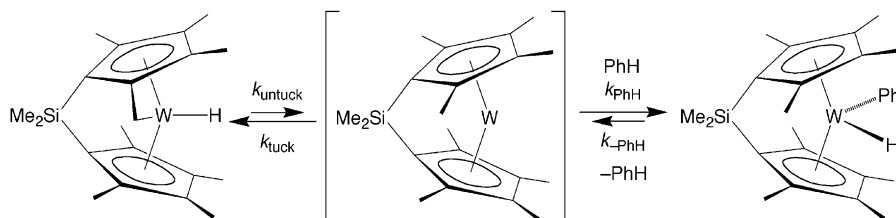
in complex Cp*(η^6-C$_5$Me$_4$CH$_2$)WH, the *ansa*-bridged tungstenocene intermediate {[Me$_2$Si(C$_5$Me$_4$)$_2$]W} is also trapped by benzene to give the phenyl hydride complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H, thereby providing another example of how a [Me$_2$Si] *ansa* bridge promotes intermolecular C−X (X = H, C, S) bond activation reactions.[7a−c] However, a kinetics analysis of the relative amounts of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$-CH$_2$)]WH and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H as a function of time demonstrates that although intermolecular oxidative addition of benzene is thermodynamically favored, intramolecular C−H bond cleavage within {[Me$_2$Si(C$_5$Me$_4$)$_2$]W} to give [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WH is actually kinetically favored, as illustrated in Figure 2. Independent kinetics experiments that (i) monitor the conversion of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$-CH$_2$)]WH to [Me$_2$Si(C$_5$Me$_4$)$_2$]W(C$_6$D$_5$)D in C$_6$D$_6$ (Scheme 4) and (ii) determine the barrier for reductive elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]W(C$_6$D$_5$)D (described in more detail below) allow the free energy surface shown in Figure 2 to be determined. The molybdenum complex [Me$_2$Si(η^5-C$_5$-Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]MoH[7b] also reacts rapidly with benzene at room temperature to give [Me$_2$Si(C$_5$Me$_4$)$_2$]Mo(Ph)H, thereby indicating that intermolecular C−H bond activation of benzene

by the molybdenocene species {[Me$_2$Si(C$_5$Me$_4$)$_2$]Mo} is also thermodynamically more favored than intramolecular C−H bond activation.

(3) Kinetic Isotope Effects and Isotope Scrambling for [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)H and Its Isotopologues. Before discussing in more detail the reductive elimination of methane from [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Me)H, it is pertinent to discuss some general aspects concerning the mechanisms of reductive elimination and oxidative addition of C−H bonds in view of the existence of σ-complex intermediates. Specifically, it is important to emphasize that the terms "reductive elimination" (re) and "oxidative addition" (oa) do not correspond to elementary steps. The terms reductive elimination and oxidative addition were introduced at a point in time when σ-complex intermediates were unknown, so additional terms are required to describe adequately the overall mechanism.[6a] Thus, as illustrated in Scheme 5 and Figure 3, reductive elimination consists of reductive coupling (rc) followed by dissociation (d), while the microscopic reverse, oxidative addition, consists of ligand association (a) followed by oxidative cleavage (oc).

The rate constant for irreversible reductive elimination (i.e. $k_a = 0$) is a composite of the rate constants for reductive
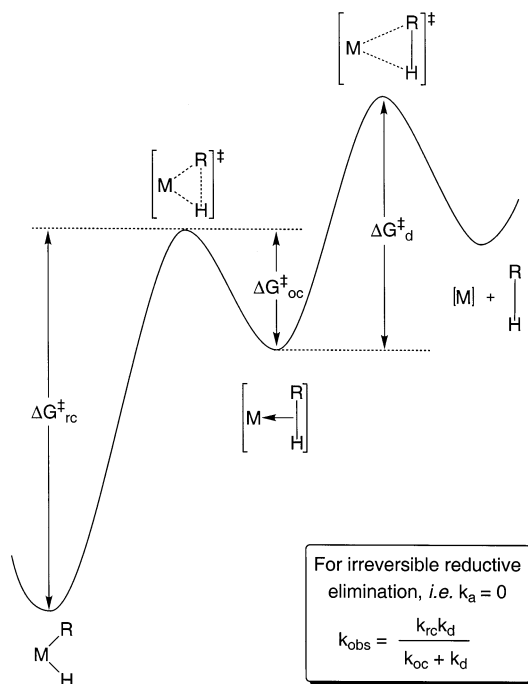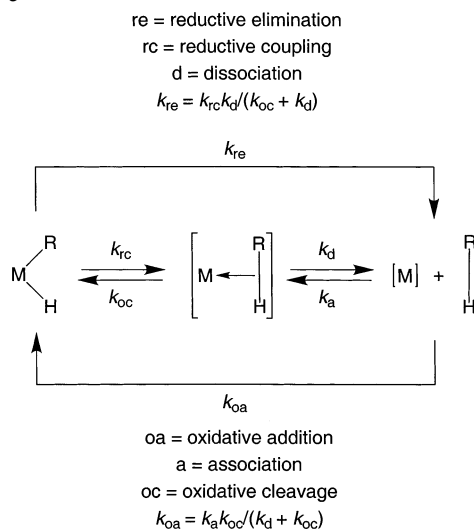
Figure 3. Free energy surface for reductive elimination of RH from a metal center via a σ-complex intermediate.
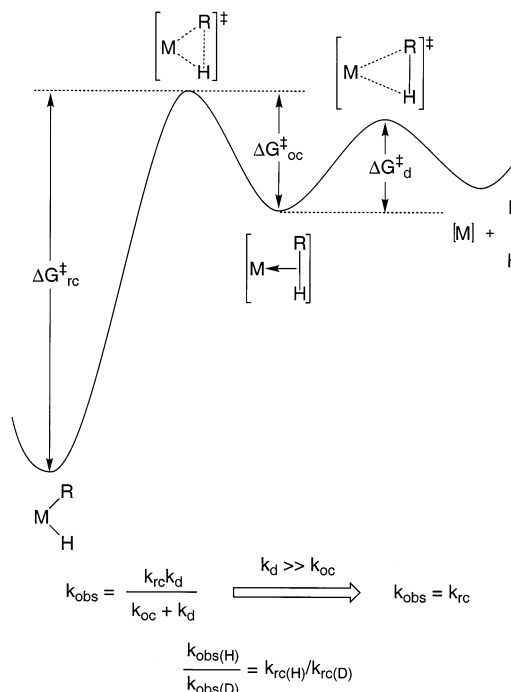
Scheme 5

Figure 4. Free energy surface for reductive elimination of RH from a metal center via a σ-complex intermediate for which $k_d \gg k_{oc}$.
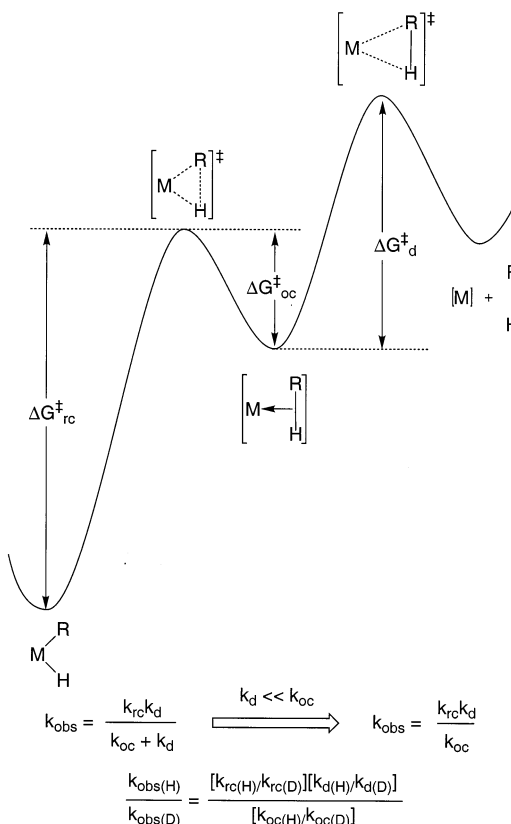

Figure 5. Free energy surface for reductive elimination of RH from a metal center via a σ-complex intermediate for which $k_d \ll k_{oc}$.

coupling (k_{rc}), oxidative cleavage (k_{oc}), and dissociation (k_d), namely, $k_{obs} = k_{rc}k_d/(k_{oc} + k_d)$. Correspondingly, the form of the energy surface depends on the relative values of the individual rate constants. There are two limiting situations: (i) if $k_d \gg k_{oc}$, the reductive coupling step becomes rate determining (Figure 4), and (ii) if $k_d \ll k_{oc}$, the dissociation of RH becomes rate determining (Figure 5). The former situation with $k_d \gg k_{oc}$ is characterized by $k_{obs} = k_{rc}$, whereas the latter situation with $k_d \ll k_{oc}$ is characterized by $k_{obs} = k_{rc}k_d/k_{oc}$. Evidence to distinguish which of the two limiting energy surfaces corresponds better to the system under investigation may be provided by measurement of the primary KIE. For example, if the reductive coupling step is rate determining (Figure 4) and the reductive coupling step exhibits a normal KIE (i.e. $k_H/k_D > 1$),[10]

one would predict a normal KIE for overall reductive elimination. On the other hand, if dissociation of RH is rate determining (Figure 5), the KIE for reductive elimination is a composite, i.e. $k_H/k_D = [k_{rc(H)}/k_{rc(D)}][k_{d(H)}/k_{d(D)}]/[k_{oc(H)}/k_{oc(D)}]$. *If* the isotope effect for dissociation of RH (i.e. $[k_{d(H)}/k_{d(D)}]$) is considered to be close to unity,[6a] the isotope effect on reductive elimination

(10) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley and Sons: New York, 1980.
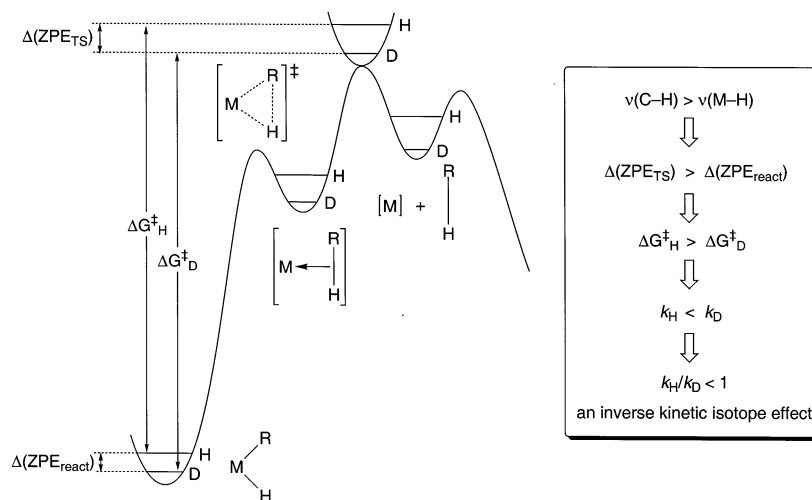
Figure 6. Origin of an inverse kinetic isotope effect for reductive elimination. The inverse kinetic isotope effect is essentially a consequence of an inverse equilibrium isotope being transferred to the rate-determining step.

is dominated by the ratio of the isotope effect on reductive coupling to that of oxidative addition, i.e. $[k_{rc(H)}/k_{rc(D)}]/[k_{oc(H)}/k_{oc(D)}]$. This ratio is identical to the *equilibrium* isotope effect (EIE) for interconversion of [M](R)H and [M](σ-RH), which would be predicted to be inverse because deuterium prefers to be located in the stronger bond, i.e C−D versus M−D.[11] On this basis, an *inverse* KIE would be predicted for the overall reductive elimination. In essence, the inverse EIE is transferred to the rate-determining step, and the overall inverse KIE for reductive elimination does not require an inverse effect for a single step (Figure 6).

The above discussion indicates that either a normal or an inverse KIE for overall reductive elimination would be predicted on the basis of whether the first or second step is rate determining. Indeed, examples of both normal[12] and inverse[13] KIEs for reductive elimination of RH are known.[6] As an illustration, complexes that exhibit normal KIEs include $(Ph_3P)_2$-Pt(Me)H (3.3),[12a] $(Ph_3P)_2Pt(CH_2CF_3)H$ (2.2),[12b] and $(Cy_2PCH_2$-$CH_2PCy_2)Pt(CH_2Bu^t)H$ (1.5),[12c] while examples of complexes that exhibit inverse KIEs include $Cp^*Ir(PMe_3)(C_6H_{11})H$ (0.7),[2] $Cp^*Rh(PMe_3)(C_2H_5)H$ (0.5),[13d] $Cp_2W(Me)H$ (0.75),[14] Cp^*_2W-(Me)H (0.70),[8] $[Cp_2Re(Me)H]^+$ (0.8),[15] $[(Me_3tacn)Rh(PMe_3)$-(Me)H]$^+$ (0.74),[16] (tmeda)Pt(Me)(H)(Cl) (0.29),[17] $[Tp^{Me_2}]$Pt-(Me)$_2$H (0.81), and $[Tp^{Me_2}]$Pt(Me)(Ph)H ($\leq$0.78).[18]

Reductive elimination of methane from $[Me_2Si(C_5Me_4)_2]W$-(CH$_3$)H and $[Me_2Si(C_5Me_4)_2]W(CD_3)D$ is also characterized by a substantial inverse KIE of 0.45(3) in benzene at 100 °C (Table

Table 2. Kinetic Isotope Effect for Elimination of Methane from $[Me_2Si(C_5Me_4)_2]W(CH_3)H$ (k_H) and $[Me_2Si(C_5Me_4)_2]W(CD_3)D$ (k_D) at 100 °C

solvent	k_H/s^{-1}	k_D/s^{-1}	k_H/k_D
C_6D_6	$3.74(5) \times 10^{-6}$	$8.35(10) \times 10^{-6}$	0.45(3)
C_6D_{12}	$4.68(17) \times 10^{-6}$	$1.00(3) \times 10^{-5}$	0.47(3)

2). Notably, the KIE is more inverse than that for the Cp$^*_2$W-(Me)H system (0.70).[8,19] As described above, the observed inverse KIE is consistent with interconversion between [Me$_2$-Si(C$_5$Me$_4$)$_2$]W(Me)H and the σ-complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W-(σ-MeH) prior to rate-determining elimination of methane.[20] Further evidence in support of a σ-complex intermediate is provided by the observation of H/D exchange between the hydride and methyl sites of the isotopologue [Me$_2$Si(C$_5$-Me$_4$)$_2$]W(CH$_3$)D. Specifically, [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D is observed to convert to [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H, prior to the elimination of methane (Scheme 6). Examples of such isotope exchange reactions are well-known.[6] A particularly striking example was reported by Green, who demonstrated that interconversion of (i) [Me$_2$C(C$_5$H$_4$)$_2$]W(CH$_3$)D and [Me$_2$C-(C$_5$H$_4$)$_2$]W(CH$_2$D)H and also (ii) [Me$_2$C(C$_5$H$_4$)$_2$]W(CD$_3$)H and [Me$_2$C(C$_5$H$_4$)$_2$]W(CD$_2$H)D occurred with no loss of methane.[9b] Keinan has likewise reported an interesting example in which [Tp]Pt(CH$_3$)H$_2$ undergoes isotopic exchange with CD$_3$OD to give [Tp]Pt(CD$_3$)D$_2$ by a mechanism that was proposed to involve initial H/D exchange of the hydride site with the solvent, followed by exchange via a σ-complex intermediate.[21,22] Keinan claimed that this was the first example of an alkyl hydride complex that underwent isotopic scrambling without concomitant liberation of alkane;[21] however, Keinan's report is predated

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(12) (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915−2916. (b) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831−1834. (c) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436−1448.
(13) For the first reports of inverse KIEs for elimination of RH (R = H,[a] Ph,[b] Cy[c,d]), see: (a) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Dalton Trans.* **1984**, 1171−1180. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620−630. (c) Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537−1550 (d) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332−7346.
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(20) Calculations on (Cp^R)$_2$M(σ-MeH) derivatives indicate that the methane in such complexes is bound asymmetrically with a single M−H−C interaction. See: (a) Green, J. C.; Jardine, C. N. *J. Chem. Soc., Dalton Trans.* **1998**, 1057−1061. (b) Green, J. C.; Harvey, J. N.; Poli, R. *J. Chem. Soc., Dalton Trans.* **2002**, 1861−1866. (c) Su, M.-D.; Chu, S.-Y. *J. Phys. Chem. A* **2001**, *105*, 3591−3597.
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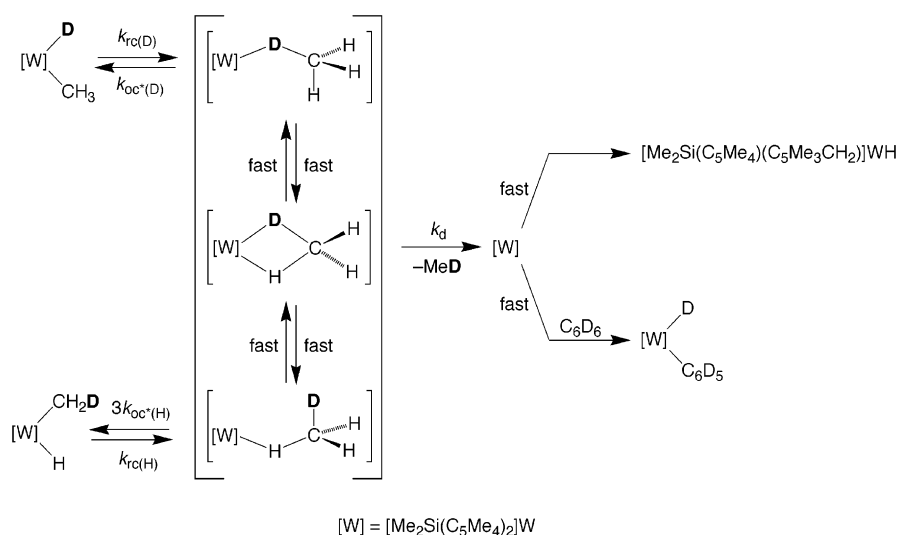
Scheme 6

[W] = [Me$_2$Si(C$_5$Me$_4$)$_2$]W

Table 3. Rate Constants for Isotope Exchange between [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H and Elimination of Methane[a]

	$k_{rc(H)}/k_{rc(D)}$ refined	$k_{rc(H)}/k_{rc(D)} = 0.45$	$k_{rc(H)}/k_{rc(D)} = 1.00$	$k_{rc(H)}/k_{rc(D)} = 2.00$	$k_{rc(H)}/k_{rc(D)} = 5.00$	$k_{rc(H)}/k_{rc(D)} = 10.00$
$k_{rc(D)}/10^{-5}$ s^{-1}	3.87(10)	5.60(28)	4.16(8)	3.66(6)	3.38(8)	3.29(8)
$k_{rc(H)}/10^{-5}$ s^{-1}	5.38(52)	2.52(13)	4.16(8)	7.32(16)	16.9(4)	32.9(8)
$k_{rc(H)}/k_{rc(D)}$	1.4(2)	0.45 (fixed)	1 (fixed)	2 (fixed)	5 (fixed)	10 (fixed)
$k_{oc*(H)}/k_{oc*(D)}$[b]	1.84(24)	0.49(4)	1.28(6)	2.72(13)	6.92(52)	13.9(1.2)
k_d	0.52(3) $k_{oc*(D)}$	0.27(3) $k_{oc*(D)}$	0.46(3) $k_{oc*(D)}$	0.57(3) $k_{oc*(D)}$	0.64(6) $k_{oc*(D)}$	0.67(7) $k_{oc*(D)}$
K[c]	4.0(7)	3.3(4)	3.9(2)	4.1(2)	4.2(4)	4.2(4)

[a] The different simulations indicate the sensitivity of the derived values as a function of the ratio $k_{rc(H)}/k_{rc(D)}$. [b] $k_{oc*(H)}$ and $k_{oc*(D)}$ correspond to the composite rate constants for oxidative coupling of C−H and C−D bonds within the equilibrating {[Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$D)} species; $k_{oc*(D)}$ is arbitrarily fixed as unity (1 s^{-1}) for the purpose of the simulation. [c] K = [[Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H]/[[Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D] = 3 [$k_{oc*(H)}/k_{oc*(D)}$]/ [$k_{rc(H)}/k_{rc(D)}$].

by Green's study.[9b] Furthermore, it is worth emphasizing that there are other examples of alkyl hydride complexes for which the barrier for exchange between the hydride and alkyl sites is considerably less than the barrier for alkane elimination.[6] For example, Heinekey has reported that site exchange within [Cp$_2$-Re(CD$_3$)H]$^+$ is much more rapid than reductive elimination, with barriers that differ by ca. 6 kcal mol^{-1}.[23] Likewise, Flood has reported that H/D exchange between hydride and hexyl ligands in the rhodium complex {(1,4,7-tacn)Rh(hexyl)D[P(OMe)$_3$]}$^+$ is significantly more rapid than elimination of hexane.[24] Furthermore, Girolami has reported an extremely interesting example of a complex for which exchange between the hydride and methyl sites is rapid on the NMR time scale, namely, [Cp*Os(dmpm)(CH$_3$)H$^+$].[25]

A kinetics analysis of the isotopic exchange within [Me$_2$Si-(C$_5$Me$_4$)$_2$]W(CH$_3$)D, and the concomitant reductive elimination of methane, was performed using the KINSIM/FITSIM simulation program.[26] The procedure used is analogous to that recently reported by Jones for the [Tp^{Me_2}]Rh(L)(Me)X system (L = CNCH$_2$Bu^t; X = H, D).[27,28] Specifically, since the σ-complex intermediates are not observed spectroscopically, it is not possible to determine absolute rate constants for oxidative cleavage or dissociation and only relative values may be derived; thus, the value for $k_{oc*(D)}$ was arbitrarily set as unity (1 s^{-1}) for the purpose of the simulation.[29] Also following Jones' procedure, the simulation assumed rapid interconversion between the various σ-complex intermediates, such that they were modeled by a single species {[Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$D)} with a single rate constant for the dissociation of methane (k_d), as illustrated in Scheme 6. Furthermore, since σ-complex intermediates are

being modeled by a single species, {[Me$_2$Si(C$_5$Me$_4$)$_2$]W-(CH$_3$D)}, the oxidative cleavage rate constants are composites for the rapidly equilibrating mixture of isotopomeric σ-complexes and are thus referred to as $k_{oc*(H)}$ and $k_{oc*(D)}$ in order to distinguish them from the values for a single species.[30]

The simulation generates the fundamental rate constants that are listed in Table 3, and a graphical representation of the simulation is presented in Figure 7. In view of correlation between pairs of rate constants, it is important to evaluate the uniqueness of the solution and the reliability of the derived results. Since we are particularly interested in the KIE for reductive coupling, i.e. $k_{rc(H)}/k_{rc(D)}$, we performed simulations to determine the sensitivity of the fit to this value. The results of simulations in which the ratio $k_{rc(H)}/k_{rc(D)}$ is fixed to predetermined values are illustrated in Figure 8. It is evident from these simulations that the fits are sensitive to the ratio

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(26) (a) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134−145. (b) Zimmerle, C. T.; Frieden, C. *Biochem. J.* **1989**, *258*, 381−387.
(27) Northcutt, T. O.; Wick, D. D.; Vetter, A. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 7257−7270.
(28) Furthermore, Bergman has performed similar simulations to analyze the kinetics of diastereomer interconversion of Cp*Ir(PMe$_3$)(2,2-dimethylcyclopropyl)H via a σ-complex intermediate. See: Mobley, T. A.; Schade, C.; Bergman, R. G. *Organometallics* **1998**, *17*, 3574−3587.
(29) It should be noted that a degree of correlation between the derived rate constants still exists even when one of the rate constants is fixed.
(30) As such, the value of $k_{oc(H*)}/k_{oc(D*)}$ [1.84(24)] derived from the simulation does not correspond to the isotope effect for oxidative cleavage, $k_{oc(H)}/k_{oc(D)}$, since it also includes the equilibrium constant for the interconversion of the isotopomeric σ-complexes.

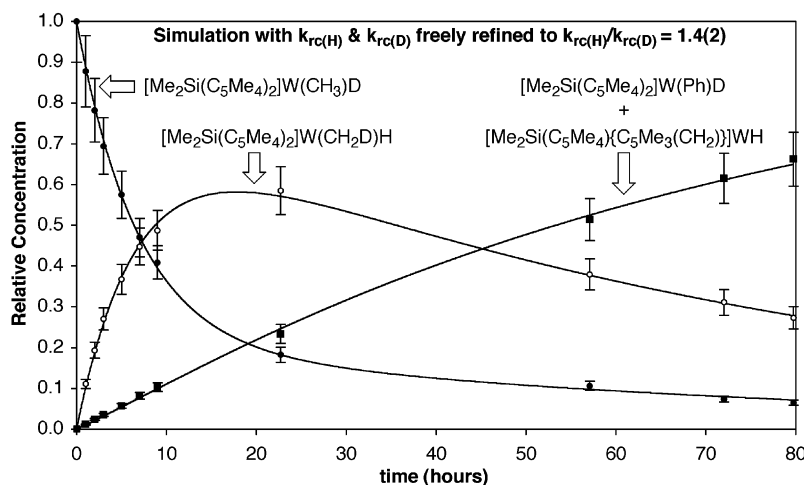**Figure 7.** Kinetic simulation of isotope exchange within $[Me_2Si(C_5Me_4)_2]W(CH_3)D$ and reductive elimination of methane. Error bars correspond to 10% uncertainty. Since the σ-complex $[Me_2Si(C_5Me_4)_2]W(\sigma\text{-}CH_3D)$ is not spectroscopically detectible, it is only possible to determine relative, and not absolute, rate constants for reactions pertaining to this species. For this reason, $k_{oc*(D)}$ was arbitrarily set as unity (1 s^{-1}).

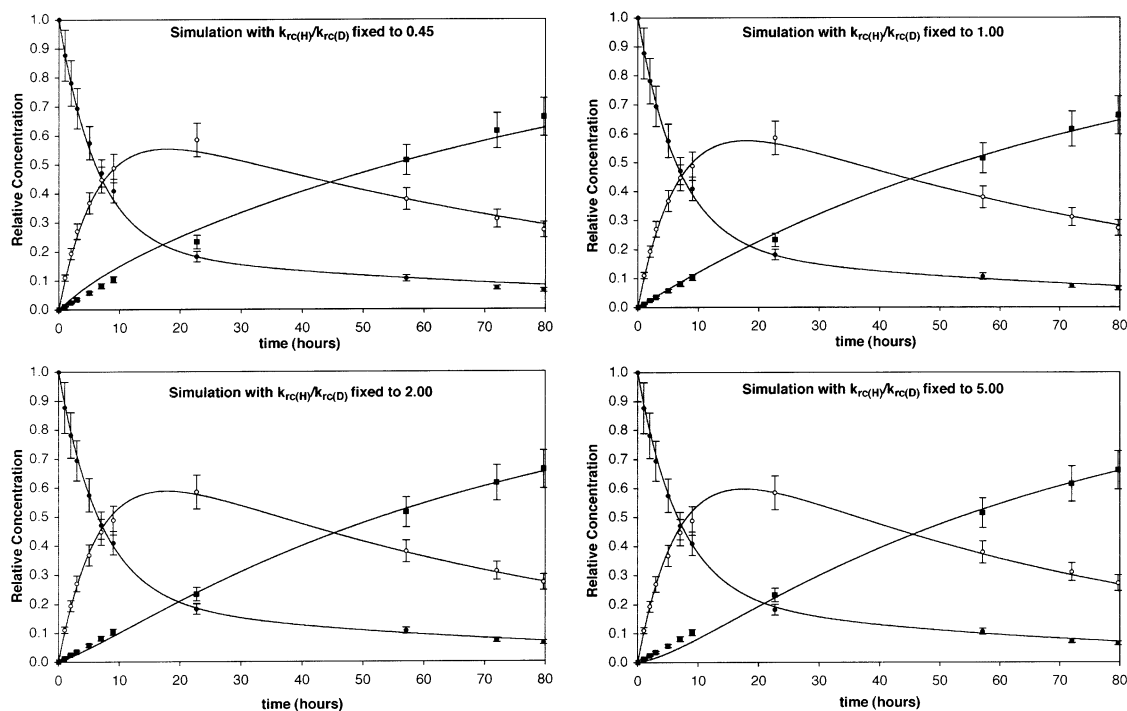**Figure 8.** Kinetic simulations of isotope exchange within $[Me_2Si(C_5Me_4)_2]W(CH_3)D$ and reductive elimination of methane in which the ratio $k_{rc(H)}/k_{rc(D)}$ is fixed to values of 0.45, 1.00, 2.00, and 5.00. Error bars correspond to 10% uncertainty. Each of these simulated fits are noticeably worse than that in which $k_{rc(H)}/k_{rc(D)}$ is allowed to freely refine to a value of 1.4 (Figure 7), as illustrated by the poor fits for the combined products of reductive elimination (solid squares). Importantly, the simulation in which the ratio $k_{rc(H)}/k_{rc(D)}$ is fixed to an inverse value of 0.45 is particularly poor, indicating that the observed kinetic isotope effect of 0.45 for elimination of methane from $[Me_2Si(C_5Me_4)_2]W(CH_3)H$ and $[Me_2Si(C_5Me_4)_2]W(CD_3)D$ is not the result of an inverse kinetic isotope effect on the reductive coupling step and thereby supports the proposal that the inverse kinetic isotope effect for the overall reductive elimination of methane is a consequence of the inverse equilibrium isotope for formation of σ-complex $[Me_2Si(C_5Me_4)_2]W(\sigma\text{-}MeH)$ being transferred to the rate-determining step.

$k_{rc(H)}/k_{rc(D)}$, especially with respect to the combined products of reductive elimination, i.e. $[Me_2Si(C_5Me_4)_2]W(Ph)H$ and $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]WH$. In particular, the fit is poor when an inverse KIE is imposed on $k_{rc(H)}/k_{rc(D)}$, as illustrated by the simulation in which $k_{rc(H)}/k_{rc(D)} = 0.45$, so chosen because this is the KIE observed for the overall reductive elimination of methane from $[Me_2Si(C_5Me_4)_2]W(CH_3)H$ and $[Me_2Si(C_5Me_4)_2]W(CD_3)D$. Deviations are also observed when the $k_{rc(H)}/k_{rc(D)}$ is fixed at values > 1.4 (the best fit value), but not as badly as when the value is forced to be inverse. Thus, the data convincingly support the notion that $k_{rc(H)}/k_{rc(D)}$ is characterized

by a *normal* isotope effect, with a value of 1.4(2). Assuming that secondary effects do not play a dominant role in the reductive coupling of $[Me_2Si(C_5Me_4)_2]W(CH_2D)H$, the value of 1.4(2) provides an estimate of the primary KIE for reductive coupling of $[Me_2Si(C_5Me_4)_2]W(Me)X$ (X = H, D) to form the σ-complex intermediate $[Me_2Si(C_5Me_4)_2]W(\sigma\text{-}XMe)$.

The rate constants corresponding to the best fit (Table 3) permit construction of the free energy surface illustrated in Figure 9, of which there are several notable features. Firstly, the barrier for elimination of methane from the σ-complex is ca. 0.5 kcal mol^{-1} greater than that for forming the σ-complex
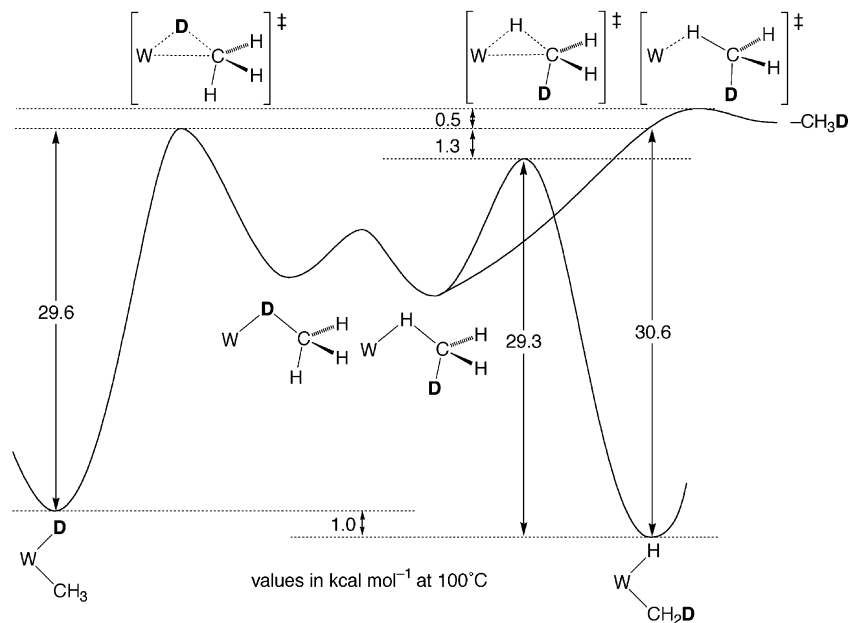
Figure 9. Free energy surface for interconversion of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H and elimination of methane at 100 °C. Note that for each pair of isotopomers, it is the one with deuterium attached to the carbon in a terminal fashion that is the lower in energy.
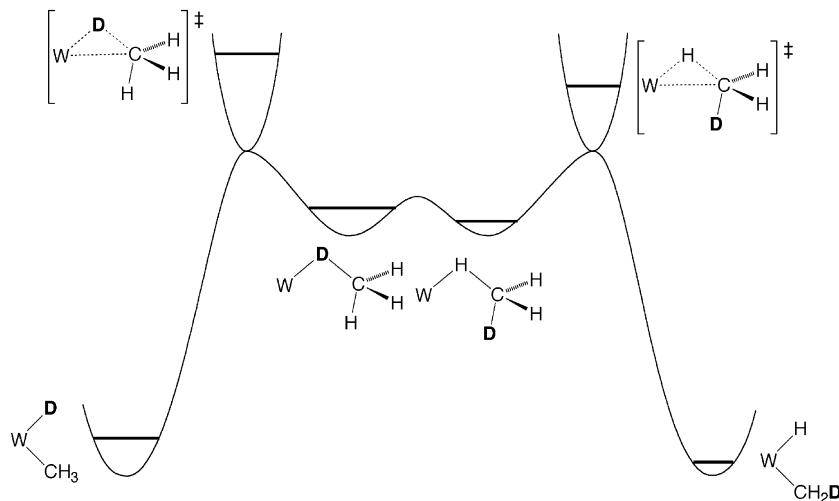

Figure 10. Enthalpic rationalization of the asymmetry of the free energy surface for isotope exchange between [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D and [Me$_2$Si-(C$_5$Me$_4$)$_2$]W(CH$_2$D)H (Figure 9). Inclusion of the zero point energy levels on the symmetric electronic energy surface (i.e. the enthalpy at 0 K) results in isotopomers with deuterium attached to carbon being lower in energy, and hence results in asymmetry on the enthalpy surface. Furthermore, a 3:1 statistical factor also plays a role in further stabilizing [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H relative to [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D on the free energy surface.

from [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D. Secondly, the free energy surface for the interconversion of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H is asymmetric. Thus, the free energy of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H is lower than that of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D due to (i) a zero point energy factor that favors the isotopomer in which deuterium is located on carbon rather than tungsten and (ii) a 3:1 statistical factor that favors the deuterium being located on the methyl, rather than hydride, site. Similar considerations also apply to the isotopomers of the σ-complex intermediates, namely, [Me$_2$Si-(C$_5$Me$_4$)$_2$]W(σ-DCH$_3$) and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-HCH$_2$D), and their corresponding transition states. The asymmetry of the free energy surface is thus clearly rationalized by considering the impact of zero point energy values and statistical factors on the symmetric electronic energy surface (i.e. the enthalpy at 0 K) for isotopic exchange (Figure 10).

It is important to note that if the reaction involved *only* interconversion of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D and [Me$_2$Si(C$_5$-Me$_4$)$_2$]W(CH$_2$D)H, without competitive loss of methane, the derived value of $k_{rc(H)}/k_{rc(D)}$ would be indeterminate, with multiple solutions existing. For example, consider the standard kinetics analysis for the approach-to-equilibrium conversion of A to B.[31] The analysis yields two independent parameters, namely, the rate constant for the approach to equilibrium (k_{app}) and the equilibrium constant (K): k_{app} is the sum of the forward and reverse rate constants, i.e. $k_{app} = k_f + k_r$, while K is their ratio, i.e. $K = k_f/k_r$. Thus, if both k_{app} and K are known, the individual values of k_f and k_r can be determined. As defined, however, k_f and k_r are composite rate constants and so it is not possible for the analysis to distinguish whether or not an

(31) *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; Espenson, J. H., Ed.; McGraw-Hill: New York, 1995.
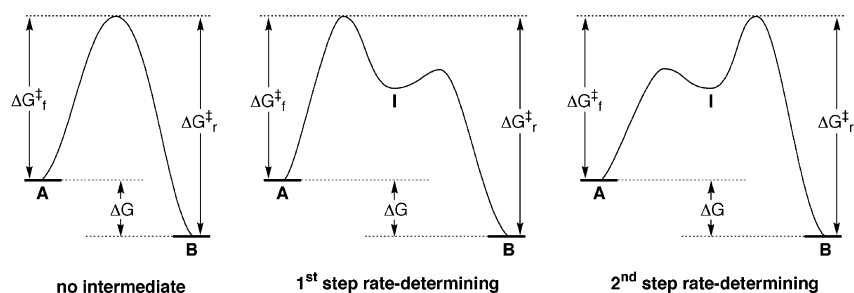
Figure 11. Illustration that approach to equilibrium kinetics is incapable of providing evidence for an intermediate. Consequently, it is indeterminate whether the first or second step is rate determining if an intermediate were to be present.
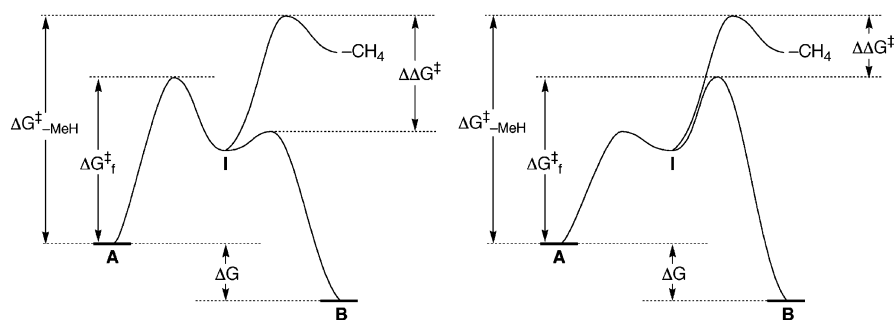

Figure 12. Illustration that the relative rates of isomerization and elimination of methane from a σ-complex intermediate are dependent on whether the first or second step of the isomerization mechanism is rate determining, for given values of ΔG, $\Delta G^{\ddagger}_f$, and $\Delta G^{\ddagger}_{-MeH}$.

intermediate exists. Consequently, should an intermediate exist, it is not possible to distinguish whether the first step or the second step is rate determining. Thus, the three situations illustrated in Figure 11 are kinetically indistinguishable on the basis of the analysis of the approach-to-equilibrium intercon-version.

For the present example involving the interconversion of $[Me_2Si(C_5Me_4)_2]W(CH_3)D$ and $[Me_2Si(C_5Me_4)_2]W(CH_2D)H$ via a σ-complex intermediate, K, k_f, and k_r are functions of $k_{oc*(H)}$, $k_{oc*(D)}$, $k_{rc(H)}$, and $k_{rc(D)}$. Specifically, $K = 3[k_{oc*(H)}/k_{oc*(D)}]/[k_{rc(H)}/k_{rc(D)}] = 3[KIE_{oc*}]/[KIE_{rc}]$, from which it is evident that it is not possible to determine the KIE for reductive coupling unless *both* the equilibrium constant for the reaction and the KIE for oxidative cleavage are known, i.e. $[KIE_{rc}] = 3[KIE_{oc*}]/K$.

It must be emphasized that the inability to determine the KIE for reductive coupling in such a situation is not a result of the exchange reaction proceeding to an equilibrium. For example, even if the forward rate of isomerization of $[Me_2Si(C_5Me_4)_2]W$-$(CD_3)H$ to $[Me_2Si(C_5Me_4)_2]W(CD_2H)D$ were to be compared with the forward rate of isomerization of $[Me_2Si(C_5Me_4)_2]W$-$(CH_3)D$ to $[Me_2Si(C_5Me_4)_2]W(CH_2D)H$, the data would still not allow for determination of the KIE for reductive coupling. The steady-state analyses of these interconversions are presented in Scheme 7, clearly demonstrating that the KIE for reductive coupling (KIE_{rc}) cannot be determined uniquely from the observed KIE measurement (KIE_{obs}) but requires a knowledge of the KIE for oxidative cleavage (KIE_{oc*}). In the absence of a value for KIE_{oc*}, it is again *not* possible to determine a value for KIE_{rc}.

It is, therefore, important to describe why the KIE for reductive coupling in the $[Me_2Si(C_5Me_4)_2]W(CH_3)D/[Me_2Si$-$(C_5Me_4)_2]W(CH_2D)H$ system is no longer indeterminate if the interconversion is competitive with loss of methane. The ability for the simulation to extract rate constants for the reductive coupling steps is made possible because the barrier for overall

Scheme 7
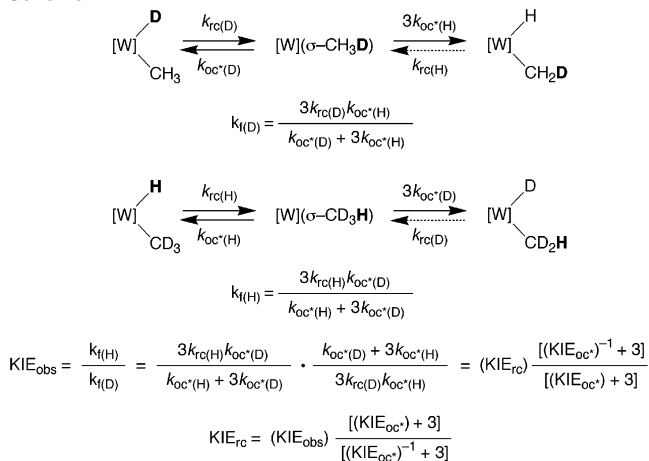
where $KIE_{rc} = k_{rc(H)}/k_{rc(D)}$ and $KIE_{oc*} = k_{oc*(H)}/k_{oc*(D)}$

reductive elimination of methane provides an additional kinetic constraint. In essence, the relative rates of methane elimination (k_d) and the formation of $[Me_2Si(C_5Me_4)_2]W(CH_2D)H$ ($k_{oc*(H)}$) from the σ-complex intermediate allows the relative energy of the transition state for oxidative-cleavage/reductive-coupling to be ascertained, as illustrated for the general situation in Figure 12. Thus, whereas a kinetics investigation of the interconversion $[Me_2Si(C_5Me_4)_2]W(CH_3)D$ and $[Me_2Si(C_5Me_4)_2]W(CH_2D)H$ alone is incapable of determining whether the first or second step is rate determining, once the relative energy of the second transition state is known, it becomes possible to determine the KIE for reductive coupling. The complete simulation therefore becomes sensitive to the ratio of $k_{rc(H)}/k_{rc(D)}$, whereas a simulation for the interconversion of only $[Me_2Si(C_5Me_4)_2]W(CH_3)D$ and $[Me_2Si(C_5Me_4)_2]W(CH_2D)H$ would be insensitive, because the ratio $k_{oc*(H)}/k_{oc*(D)}$ would merely adjust to maintain a constant value for K.

The observation of a normal kinetic isotope effect for reductive coupling within $[Me_2Si(C_5Me_4)_2]W(Me)H$ is significant because it supports the notion that the inverse nature of the KIE for the reductive elimination of methane is *not* a manifestation of an inverse KIE for a single step in the transformation but is rather associated with an inverse *equilibrium* isotope effect. Of direct relevance to this issue, Jones has recently demonstrated that the EIE for the interconversion of $[Tp^{Me_2}]Rh(L)(Me)X$ and $[Tp^{Me_2}]Rh(L)(\sigma\text{-XMe})$ is *inverse* because the KIE for oxidative cleavage is greater than that for reductive coupling, with both values being normal.[27]

Although the notion that the reductive coupling of a methyl–hydride complex is characterized by a normal primary kinetic deuterium isotope effect is in line with the common understanding of KIEs,[6] it has recently been proposed that the reductive coupling for $[Tp]Pt(Me)H_2$ is characterized by an *inverse* KIE.[21] The experimental study involved comparing (i) the rate constant for deuterium incorporation into the methyl group of $[Tp]Pt(CH_3)H_2$ when dissolved in CD_3OD (k_D) with (ii) the rate constant for hydrogen incorporation into the methyl group of $[Tp]Pt(CD_3)D_2$ when dissolved in CD_3OH (k_H). The mechanism proposed involved rapid H/D exchange between the solvent and hydride site, followed by a slower isomerization via a σ-complex intermediate. The observed kinetic isotope effect, $(k_H/k_D)_{obs} = KIE_{obs} = 0.76$, was proposed to correspond to that for reductive coupling. However, as described above, it is not possible to extract the KIE for reductive coupling from such a measurement because the KIE for oxidative cleavage is unknown.[32] Assigning the observed KIE to that for reductive coupling is only possible if KIE_{oc*} is unity.

The observed inverse KIE for $[Tp]Pt(CH_3)H_2$ can be readily explained on the basis of normal KIEs for both reductive coupling and oxidative cleavage steps, as illustrated in Figure 13. In essence, whereas the barrier for isotope exchange of $[Tp]Pt(CH_3)D_2$ is *equal* to the barrier for reductive coupling, the barrier for isotope exchange of $[Tp]Pt(CD_3)H_2$ is *greater* than the barrier for reductive coupling, since it is now the second step that becomes rate determining, as illustrated in Figure 13. The KIE for isotope exchange of $[Tp]Pt(CD_3)H_2$ is thus a composite and is *not* that for reductive coupling.[33] Thus, the reported "kinetic isotope effect" for reductive coupling of $[Tp]Pt(CH_3)X_2$ (X = H, D) is not actually a KIE for a single step, but more closely corresponds to the *equilibrium constant* for the exchange reaction because it is merely the ratio of the forward and reverse rate constants. An inverse equilibrium constant would be expected for such a reaction since deuterium prefers to be located in the stronger bond, i.e. C–D versus Pt–D.[11]

Although the fact that KIE_{obs} is a function of both KIE_{rc} and KIE_{oc*} was not considered in the original papers,[21] an expression that directly relates KIE_{obs} to KIE_{rc} and KIE_{oc} has subsequently been presented, namely, $KIE_{obs} = KIE_{rc}[(KIE_{oc*})^{-1} + 9]/[(KIE_{oc*}) + 9]$.[34,35] This expression clearly invalidates the original

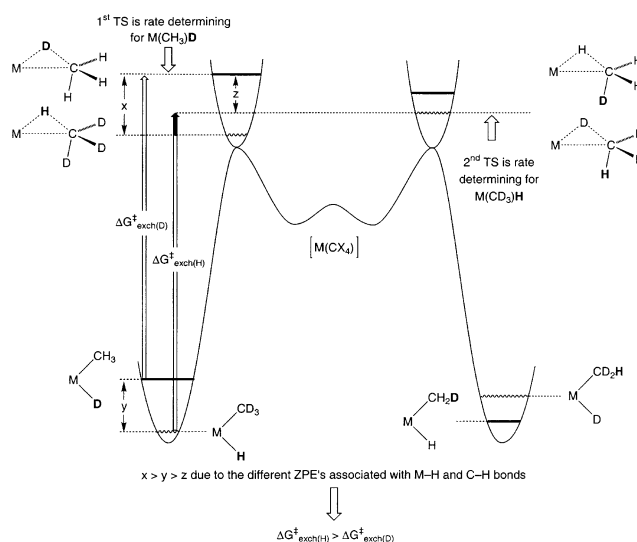**Figure 13.** Illustration that the forward rate for exchange of a $[M(CH_3)D]$ complex is faster than that for a $[M(CD_3)H]$ derivative on the basis of zero point energy differences on the electronic energy surface (i.e. the enthalpy at 0 K). For the $[M(CH_3)D]$ system the zero point energies are illustrated with bold lines, while the $[M(CD_3)H]$ system the zero point energies are illustrated with curly lines. For $[M(CH_3)D]$, it is the first transition state (corresponding to reductive coupling) that is rate determining, whereas for $[M(CD_3)H]$ it is the second transition state (corresponding to oxidative cleavage) that becomes rate determining because hydrogen, rather than deuterium, is now attached to carbon on a terminal site in the transition state.

proposal that the KIE for reductive coupling had been determined to be inverse with a value of 0.76.[21] In an effort to determine what value of KIE_{oc*} would cause KIE_{rc} to be ≤ 1, the authors plotted KIE_{rc} versus KIE_{oc*} for the function $KIE_{rc} = KIE_{obs}[(KIE_{oc*}) + 9]/[(KIE_{oc*})^{-1} + 9]$, where KIE_{obs} has the experimental value of 0.76.[34] On the basis of this plot, an inverse value of KIE_{rc} would be predicted for a value of $KIE_{oc*} < 3.25$. However, the expression used, $KIE_{rc} = KIE_{obs}[(KIE_{oc*}) + 9]/[(KIE_{oc*})^{-1} + 9]$, is incorrect. Specifically, the constant "9" is erroneous and should be "3", as illustrated in Scheme 7. The correct value of 3 for the first exchange corresponds to a statistical factor for cleaving the C–H versus C–D bond in a rapidly equilibrating mixture of $M(\sigma\text{-}CH_3D)$ σ-complexes (and correspondingly that for cleaving the C–D versus C–H bond in a mixture of $M(\sigma\text{-}CD_3H)$ σ-complexes); the incorrect value of 9 is a consequence of erroneously applying this statistical factor twice.[34,36] Using the correct statistical factor of 3 for the first exchange, an inverse value of KIE_{rc} would be predicted only for a value of $KIE_{oc*} < 1.72$ which is substantially less than the proposed value of 3.25 (Figure 14). Furthermore, the originally reported value of 0.76 for KIE_{rc} is only obtained when $KIE_{ox*} = 1$. It is, therefore, evident that the experiment purported to determine an inverse kinetic isotope effect of 0.76 for the reductive coupling of $[Tp]Pt(Me)X_2$ (X = H, D) is erroneous[32] and that the system does not provide the claimed unprecedented opportunity to study the initial step of reductive coupling in alkyl hydride compounds.[34]

(4) Kinetic Isotope Effects for Reductive Elimination of Benzene from $[Me_2Si(C_5Me_4)_2]M(Ph)H$ (M = Mo, W). In

(32) For further criticism of the proposed KIE for reductive coupling, see ref 6a.

(33) It should also be pointed out that, even if the reductive coupling for $[Tp]Pt(CH_3)H_2$ were to be characterized by an inverse kinetic isotope effect, the problem would still exist because isotopic exchange of $[Tp]Pt(CH_3)D_2$ would then be a composite.

(34) Lo, H. C.; Haskel, A.; Kapont, M.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 12626.

(35) The symbols used here differ slightly from those of ref 34. Specifically, $kie^{red} = KIE_{rc}$ and $kie^{ox} = KIE_{oc*}$.

(36) It should also be noted that the analysis described in ref 34 (eq 17) considers only the first cycle of exchange, i.e. $Pt–CH_3$ to $Pt–CH_2D$ and $Pt–CD_3$ to $Pt–CD_2H$, whereas the experimental study examined complete exchange. While a more complex analysis is required to determine the exact relationship between KIE_{rc} and KIE_{oc*} for a given value of KIE_{obs}, the value of KIE_{rc} will, nevertheless, remain indeterminate unless KIE_{oc*} is known.
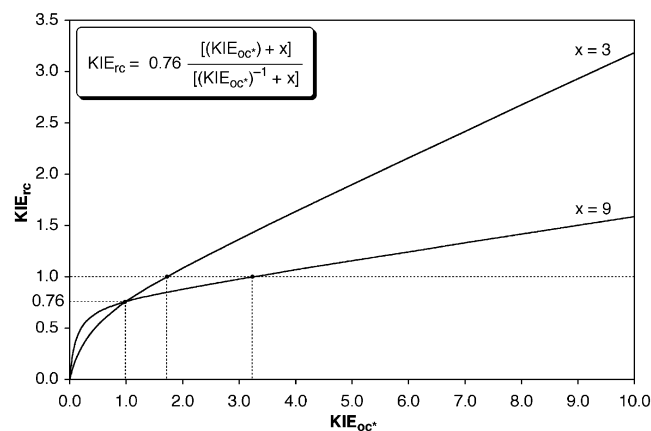
Figure 14. Relationship between KIE_{rc} and KIE_{oc*} for comparison of the first exchange for $M(CH_3)D$ and $M(CD_3)H$ systems for a fixed value of $KIE_{obs} = 0.76$. The two lines show the relationships for statistical factors of $x = 3$ and $x = 9$, thereby demonstrating that an inverse KIE_{rc} for the correct statistical factor of 3 is only observed if $KIE_{oc*} < 1.72$. Furthemore, a value of $KIE_{rc} = 0.76$ is only observed when $KIE_{oc*} = 1$.
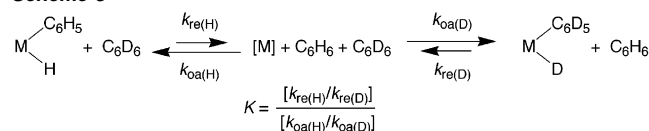
Scheme 8

Table 4. Rate Constants for Reductive Elimination of Benzene from $[Me_2Si(C_5Me_4)_2]W(C_6H_5)H$ and $[Me_2Si(C_5Me_4)_2]W(C_6D_5)D$ in C_6X_6 (X = H, D) and C_6X_6/C_6D_{12} at 182 °C

$[C_6X_6]$/M	k_H/s^{-1}	k_D/s^{-1}	k_H/k_D
neat[a]	$6.49(14) \times 10^{-7}$	$1.15(3) \times 10^{-6}$	0.56(3)
0.22	$5.35(27) \times 10^{-7}$	$8.17(84) \times 10^{-7}$	0.65(10)

[a] 11.1 M C_6H_6; 11.3 M C_6D_6.

addition to studying the reductive elimination of methane, we have also investigated the reductive elimination of benzene from $[Me_2Si(C_5Me_4)_2]W(Ph)H$. Whereas the reductive elimination of methane is irreversible, the reductive elimination of benzene is reversible and may therefore be conveniently studied by observing isotopic exchange with C_6D_6 solvent (Scheme 8). A kinetics analysis indicates that the barrier for reductive elimination of benzene is substantially higher than that for methane; for example, $k_{MeH}/k_{PhH} \approx 10^4$ at 182 °C.[37]

The KIE for reductive elimination of benzene from $[Me_2Si(C_5Me_4)_2]W(C_6H_5)H$ and $[Me_2Si(C_5Me_4)_2]W(C_6D_5)D$ is inverse, with $k_H/k_D = 0.65(10)$ at 182 °C (Table 4). By analogy with the KIE for reductive elimination of methane [0.45(3) at 100 °C], the inverse isotope effect for reductive elimination of benzene is also consistent with the existence of an intermediate with an intact C−H bond prior to rate-determining loss of benzene (Figure 15); further evidence for an intermediate, discussed in more detail below, is the observation that the intermolecular and intramolecular KIEs for oxidative addition of benzene are different. Two possibilities exist for this intermediate with an intact C−H bond, namely, (i) an η^2-π-complex in which the benzene coordinates by a C═C double bond and (ii) a σ-complex in which the benzene coordinates via a C−H bond. In support of the former possibility, Jones and Perutz have provided considerable evidence that an η^2-π-

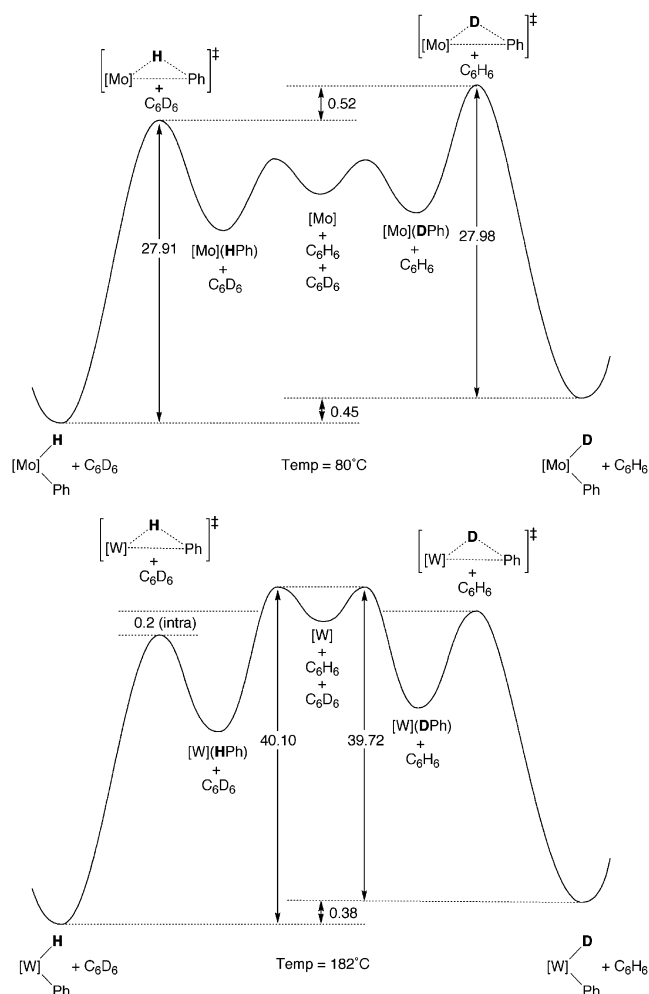(37) The rate constant for $[Me_2Si(C_5Me_4)_2]W(Me)H$ at 182 °C was determined by extrapolation.

Figure 15. Comparison of the free energy surfaces for reductive elimination of benzene from $[Me_2Si(C_5Me_4)_2]M(C_6H_5)H$ and $[Me_2Si(C_5Me_4)_2]M(C_6D_5)D$ in C_6D_{12} (M = Mo at 80 °C, W at 182 °C). Energies in kcal mol^{-1}.

complex mediates the oxidative addition and reductive elimination of benzene from $Cp*Rh(PMe_3)(Ph)H$.[38,39] With respect to the viability of a σ-complex intermediate, Bergman has postulated that η^2-π-benzene coordination is *not* part of the reaction coordinate for the oxidative addition of benzene to $[Cp*Ir(PMe_3)]$ and has proposed that a benzene σ-complex is responsible for benzene precoordination.[40,41] Density functional theory (DFT) calculations (described in more detail below) indicate that reductive coupling of $[Me_2Si(C_5Me_4)_2]W(Ph)H$

(38) See, for example: (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814−4819. (b) Chin, R. M.; Dong, L. Z.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685−7695. (c) Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 266−269. (d) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928−930. (e) Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. *Organometallics* **1992**, *11*, 871−876.

(39) For other recent examples of η^2-benzene complexes, see: (a) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724−12725. (b) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846−10855. (c) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038−1040.

(40) Peterson, T. H.; Golden, J. T.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 455−462.

(41) Further support for a benzene σ-complex intermediate is provided by the structural characterization of a derivative of a bidentate phosphine ligand that exhibits an η^2-H−Ar interaction, see: Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539−12544.
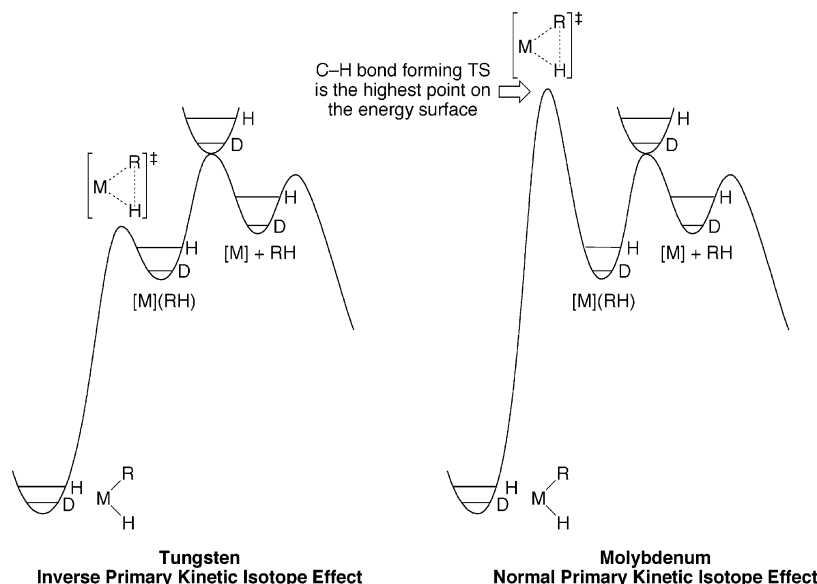
Figure 16. Explanation for a normal kinetic isotope effect for elimination of RH from molybdenum but an inverse kinetic isotope effect for tungsten. A normal isotope effect is observed for molybdenum because the rate-determining step is reductive coupling. For clarity, no distinction is made between a benzene σ-complex and an η^2-π-benzene complex for the situation in which R = Ph.

results *directly* in the formation of the benzene σ-complex [Me$_2$-Si(C$_5$Me$_4$)$_2$]W(σ-HPh) but that this species is thermodynamically unstable with respect to isomerization to the η^2-π-complex [Me$_2$-Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$).

A most interesting difference in the reductive elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H and [Me$_2$Si(C$_5$Me$_4$)$_2$]-Mo(Ph)H is that an inverse KIE is *not* observed for the molybdenum system. Specifically, reductive elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]Mo(Ph)H is characterized by a *normal* KIE, with $k_H/k_D = 1.14(10)$. It is important to emphasize that the observation of a normal kinetic isotope for reductive elimination does not imply the nonexistence of either a σ-complex or an η^2-π-benzene intermediate for the molybdenum system, but rather indicates that the reductive coupling step is the rate-determining step of the reductive elimination reaction. In contrast, the reductive coupling step is not rate determining for the tungsten system, and a subsequent step (which could be either isomerization to the η^2-π-benzene complex or dissociation of benzene) becomes rate determining (Figure 16).

It is interesting to contrast the normal KIE for the reductive coupling step of [Me$_2$Si(C$_5$Me$_4$)$_2$]Mo(Ph)H with the inverse KIE that Jones has reported for Cp*Rh(PMe$_3$)(Ph)H of 0.52.[38a] A possible rationalization of the difference is that the KIE for reductive coupling of [Me$_2$Si(C$_5$Me$_4$)$_2$]Mo(Ph)H corresponds more to that for formation of a σ-complex intermediate, whereas the KIE for Cp*Rh(PMe$_3$)(Ph)H corresponds to the formation of an η^2-π-benzene intermediate. If the formation of an η^2-π-benzene complex in the rhodium system were to be preceded by the reversible formation of a σ-complex intermediate, the observed isotope effect for reductive coupling would then be a composite of the two steps. Alternatively, it is possible that the reductive coupling of Cp*Rh(PMe$_3$)(Ph)H to give the η^2-π-benzene intermediate occurs in a single step, such that the KIE would not be expected to be the same as that for forming a σ-complex intermediate.

(5) Kinetic Isotope Effects for Oxidative Addition of Benzene to {[Me$_2$Si(C$_5$Me$_4$)$_2$]M} (M = Mo, W). To substantiate the proposal that the rate-determining steps for reductive

Table 5. Rate Constants Pertaining to the Reaction of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WH with C$_6$D$_6$ at 100 °C

	k		k
k_{untuck}	$5.99(32) \times 10^{-6}$ s^{-1}	$k_{\text{tuck}}/k_{\text{PhD}}{}^a$	15.1(1.3) M
$k_{\text{tuck}}/\{k_{\text{PhD}}[\text{C}_6\text{D}_6]\}$	1.34(11)	$k_{\text{obsd}}{}^b$	$2.56(35) \times 10^{-6}$ s^{-1}

^{a} $k_{\text{tuck}}/k_{\text{PhD}}$ is derived from the value $k_{\text{tuck}}/k_{\text{PhD}}[\text{C}_6\text{D}_6]$ using 11.3 M as the concentration of C$_6$D$_6$. ^{b} k_{obs} for the conversion of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]WH to [Me$_2$Si(C$_5$Me$_4$)$_2$]W(C$_6$D$_5$)D is defined by $k_{\text{untuck}}k_{\text{PhD}}[\text{C}_6\text{D}_6]/\{k_{\text{tuck}} + k_{\text{PhD}}[\text{C}_6\text{D}_6]\}$, i.e. $k_{\text{untuck}}/\{1 + (k_{\text{tuck}}/k_{\text{PhD}}[\text{C}_6\text{D}_6])\}$.

Table 6. Rate Constants^a for the Reaction of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]MoH with C$_6$D$_6$

T/°C	k_{obs}/s^{-1}	T/°C	k_{obs}/s^{-1}
5	$4.21(4) \times 10^{-5}$	25	$6.18(16) \times 10^{-4}$
15	$1.86(4) \times 10^{-4}$	35	$2.01(9) \times 10^{-3}$
$\Delta H^{\ddagger} = 21.2(5)$ kcal mol^{-1}; $\Delta S^{\ddagger} = 2(2)$ e.u.			

^{a} $k_{\text{obs}} = k_{\text{untuck}}k_{\text{PhD}}[\text{C}_6\text{D}_6]/\{k_{\text{tuck}} + k_{\text{PhD}}[\text{C}_6\text{D}_6]\}$.

elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]Mo(Ph)H and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H are different, we have probed the nature of the energy surface in more detail by studying the microscopic reverse. Specifically, KIEs for oxidative addition of benzene to the metallocenes {[Me$_2$Si(C$_5$Me$_4$)$_2$]M} were determined by competition experiments using the tuck-in complexes [Me$_2$Si(η^5-C$_5$Me$_4$)(η^6-C$_5$Me$_3$CH$_2$)]MH (M = Mo, W) as sources of the metallocenes {[Me$_2$Si(C$_5$Me$_4$)$_2$]M}, as illustrated in Scheme 4. In this regard, it is important to note that the temperatures required to generate {[Me$_2$Si(C$_5$Me$_4$)$_2$]M} from [Me$_2$Si(C$_5$Me$_4$)(C$_5$Me$_3$CH$_2$)]MH (e.g. 100 °C for M = W) are much lower than those for effecting reductive elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]M(Ph)H (e.g. 182 °C for M = W), so that competition experiments with C$_6$H$_6$/C$_6$D$_6$ mixtures allow the intermolecular KIEs for oxidative addition to be determined in the absence of thermodynamic equilibration (Tables 5 and 6).

An independent assessment of the KIEs for the oxidative addition and reductive elimination of benzene is provided by measurement of the equilibrium constants for the isotope exchange reaction between [Me$_2$Si(C$_5$Me$_4$)$_2$]M(Ph)H and C$_6$D$_6$

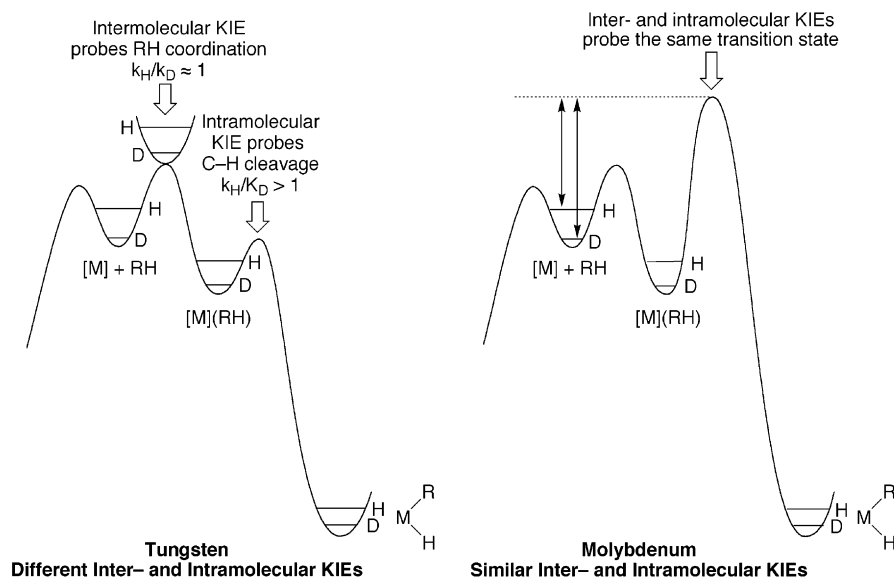**Figure 17.** Different kinetic isotope effects for oxidative addition of benzene to $\{[Me_2Si(C_5Me_4)_2]Mo\}$ and $\{[Me_2Si(C_5Me_4)_2]W\}$. A significant kinetic isotope effect is observed for addition to $\{[Me_2Si(C_5Me_4)_2]Mo\}$ because the rate-determining step involves cleavage of the C−H(D) bond, whereas no isotope effect is observed for $\{[Me_2Si(C_5Me_4)_2]W\}$ since the rate-determining step involves coordination of benzene. However, an intramolecular kinetic isotope effect is observed for reaction of $C_6H_3D_3$ with $\{[Me_2Si(C_5Me_4)_2]W\}$ because it now probes the product-forming step, rather than the rate-determining step. For molybdenum, the inter- and intramolecular kinetic isotope effects are similar because they probe the same transition state.

Table 7. Isotope Effects[a] for $[Me_2Si(C_5Me_4)_2]M(Ph)H$ (T = 80 °C for Mo and 182 °C for W)

	Mo	W
$k_{re(H)}/k_{re(D)}$	1.14(10)	0.65(10)
$[k_{oa(H)}/k_{oa(D)}]_{inter}$	2.1(2)	1.0(1)
$[k_{oa(H)}/k_{oa(D)}]_{intra}$	2.6(2)	1.4(2)
$K_{calc} = [k_{re(H)}/k_{re(D)}]/[k_{oa(H)}/k_{oa(D)}]_{inter}$	0.54	0.65
K_{obs}	0.53(2)	0.66(5)

[a] Since the rate-determining steps are different for Mo and W, the observed composite rate constants for reductive elimination [$k_{re} = k_{rc}k_d/(k_{oc} + k_d)$] and oxidative addition [$k_{oa} = k_ak_{oc}/(k_d + k_{oc})$] correspond to different approximations, as illustrated in Figures 4 and 5. The only direct correspondences with single rate constants are as follows: $k_{re(H)}/k_{re(D)} = k_{rc(H)}/k_{rc(D)}$ (for Mo) and $[k_{oa(H)}/k_{oa(D)}]_{inter} = k_{a(H)}/k_{a(D)}$ (for W).

Table 8. Kinetic Isotope Effects for Oxidative Addition of Benzene by Competitive Trapping of $\{[Me_2Si(C_5Me_4)_2]M\}$ (M = Mo, W)

M	C_6X_6	$T/°C$	k_H/k_D
	Intermolecular		
Mo	1:1 C_6H_6/C_6D_6	0	3.1(1)
Mo	1:1 C_6H_6/C_6D_6	25	2.7(1)
Mo	1:1 C_6H_6/C_6D_6	80	2.1(2)[a]
W	1:1 C_6H_6/C_6D_6	100	1.0(1)
	Intramolecular		
Mo	1,3,5-$C_6H_3D_3$	0	3.2(1)
Mo	1,3,5-$C_6H_3D_3$	25	3.0(2)
Mo	1,3,5-$C_6H_3D_3$	80	2.6(2)[a]
W	1,3,5-$C_6H_3D_3$	100	1.4(2)

[a] Extrapolated.

(Scheme 8). Specifically, the equilibrium constant (K) for this reaction corresponds directly with the EIE for reductive elimination of benzene from $[Me_2Si(C_5Me_4)_2]M(C_6H_5)H$ and $[Me_2Si(C_5Me_4)_2]M(C_6D_5)D$, as defined by $K_H/K_D = [k_{re(H)}/k_{re(D)}]/[k_{oa(H)}/k_{oa(D)}]_{inter}$. Examination of Table 7 indicates that there is very close correspondence between the two methods, thereby substantiating the derived KIEs.

Significantly, the oxidative addition of benzene to the molybdenocene and tungstenocene fragments is characterized by very different KIEs (Table 7). Thus, a substantial KIE is observed for oxidative addition to the molybdenocene species, whereas no KIE is observed for oxidative addition to the tungstenocene analogue (Table 7). These KIEs are consistent with the energy surfaces illustrated in Figures 15 and 17. Specifically, a significant KIE is observed for addition to $\{[Me_2Si(C_5Me_4)_2]Mo\}$ because the rate-determining step involves cleavage of the C−H bond, whereas no isotope effect is observed for $\{[Me_2Si(C_5Me_4)_2]W\}$ since the rate-determining step only involves coordination of benzene (Figure 17); by comparison to the KIE for C−H cleavage, coordination that does not involve significant weakening of the C−H bond (be it via a benzene σ-complex or a η^2-π-complex) would not be expected to result in a significant KIE.

Although the intermolecular C_6H_6/C_6D_6 competition experiment is incapable of probing the step involving oxidative cleavage of the C−H bond for the tungsten system, such information can be obtained by an intramolecular competition experiment employing selectively deuterated benzene, i.e. 1,3,5-$C_6H_3D_3$. Intramolecular KIEs of this type have the potential of specifically probing the C−H cleavage step. However, it must be emphasized that if the cleavage step occurs after the rate-determining step, the intramolecular KIE only corresponds to the C−H cleavage step *if* the H/D benzene sites in the intermediate are either equivalent or interchange rapidly. If the H/D benzene sites in the intermediate are not capable of being rendered equivalent, the intramolecular KIE would then correspond to the intermolecular KIE. The observation that the intramolecular KIE of 1.4(2) for addition of benzene to $\{[Me_2Si(C_5Me_4)_2]W\}$ is distinct from the intermolecular KIE of 1.0(1) (Tables 7 and 8) indicates clearly that the isotope effects are probing different steps and thereby indicates the existence of an intermediate (Figure 17). The requirement that H/D benzene sites are equivalent may be achieved by either (i) the initial formation of a benzene η^2-π-complex or (ii) facile interconversion between the benzene σ-complex and the η^2-π-complex. For both situations, the intramolecular KIE corre-

sponds specifically to the transformation from the species that has equivalent H/D benzene sites, i.e. an η^2-π-benzene complex. Therefore, the intramolecular KIE of 1.4(2) for the addition of 1,3,5-$C_6H_3D_3$ to $\{[Me_2Si(C_5Me_4)_2]W\}$ reflects a composite of the η^2-π-benzene to σ-complex isomerization and oxidative cleavage. Jones has also reported intermolecular ($k_H/k_D = 1.05$) and intramolecular ($k_H/k_D = 1.4$) KIEs for oxidative addition of benzene to the $\{Cp*Rh(PMe_3)\}$ fragment that are very similar to those for $\{[Me_2Si(C_5Me_4)_2]W\}$ and has likewise interpreted the difference between intermolecular and intramolecular KIEs as providing evidence for an η^2-π-benzene intermediate.[38a]

An intramolecular KIE of 2.6(2) is also observed for oxidative addition of 1,3,5-$C_6H_3D_3$ in the molybdenum system, which also corresponds to a transformation from the η^2-π-benzene complex, i.e. a composite of isomerization to the σ-complex and oxidative cleavage. In contrast to the tungsten system, however, where no intermolecular KIE is observed, a comparable intermolecular KIE is observed for the molybdenum system because the two KIEs probe the same C–H bond cleavage transition state (Table 7 and Figure 17).[42] In this regard, Bergman has reported that oxidative addition of benzene to the $\{Cp*Ir(PMe_3)\}$ fragment also exhibits similar intramolecular ($k_H/k_D = 1.15$) and intermolecular ($k_H/k_D = 1.22$) KIEs.[40]

The equilibrium constant for the interconversion of $[Me_2Si(C_5Me_4)_2]Mo(C_6H_2D_2)D$ and $[Me_2Si(C_5Me_4)_2]Mo(C_6H_2D_3)H$ [1.96(8)][43] corresponds to the EIE for C–H versus C–D cleavage of $C_6H_3D_3$ by $\{[Me_2Si(C_5Me_4)_2]Mo\}$. Likewise, this intramolecular EIE corresponds directly to the EIE for the conversion of the η^2-π-complex to the phenyl hydride.[44] Correspondingly, the EIE for the reverse reaction, i.e. the formation of $[Me_2Si(C_5Me_4)_2]Mo(\eta^2$-$\pi$-$C_6H_6)$ from $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$, is 0.51(2). This value is in accord with the inverse EIEs reported by Jones for the interconversion of (i) $Cp*Rh(PMe_3)(Ph)H$ and $Cp*Rh(PMe_3)(\eta^2$-π-$C_6H_6)$ [$K_H/K_D = 0.37$][38a] and (ii) $[Tp^{Me_2}]Rh(L)(Me)H$ and $[Tp^{Me_2}]Rh(L)(\sigma$-HMe) [$K_H/K_D = 0.5$].[27]

The combined study of the kinetic and equilibrium isotope effects pertaining to the reductive elimination of benzene from $[Me_2Si(C_5Me_4)_2]M(Ph)H$, and the microscopic reverse, oxidative

addition of the C–H bond of benzene to $\{[Me_2Si(C_5Me_4)_2]M\}$, illustrates a significant difference in the energy surface for the molybdenum and tungsten systems. It is likely that this difference will also be observed for other $[Me_2Si(C_5Me_4)_2]M$-(R)H derivatives. The principal distinction is concerned with the relative barriers for oxidative cleavage within the hydrocarbon adduct $[Me_2Si(C_5Me_4)_2]M(RH)$, be it a σ-complex or η^2-π-complex, *versus* dissociation of RH. To a certain extent, the relative barriers for oxidative cleavage within $[Me_2Si(C_5Me_4)_2]M(RH)$ versus dissociation of RH reflect the difference in energies of the $[Me_2Si(C_5Me_4)_2]M(R)H$ and $\{[Me_2Si(C_5Me_4)_2]M\}$ species, which is greater for tungsten due to the stronger W–X versus Mo–X bonds.[45,46] Stabilization of $\{[Me_2Si(C_5Me_4)_2]M\}$ would be expected to reduce the barrier for dissociation of RH from $[Me_2Si(C_5Me_4)_2]M(RH)$, with the result that the transition state for C–H oxidative cleavage becomes the highest point on the energy surface (Figure 18, right-hand side). Correspondingly, stabilization of $[Me_2Si(C_5Me_4)_2]M(R)H$ would be expected to lower the barrier for oxidative cleavage within $[Me_2Si(C_5Me_4)_2]M(RH)$, with the result that the transition state for dissociation of RH becomes the highest point on the energy surface (Figure 18, left-hand side). Since oxidative addition to $\{[Me_2Si(C_5Me_4)_2]W\}$ is more exothermic than that to $\{[Me_2Si(C_5Me_4)_2]Mo\}$, the above provides a simple rationalization for a change in the rate-determining step and a difference in the KIEs for two otherwise very similar systems.

(6) Computational Evidence That a Benzene σ-Complex Precedes the Formation of an η^2-π-Benzene Complex during Reductive Elimination of Benzene from $[Me_2Si(C_5Me_4)_2]W$-(Ph)H. To address the issue of whether it is a benzene σ-complex or an η^2-π-complex that is on the direct energy surface for reductive coupling of $[Me_2Si(C_5Me_4)_2]W(Ph)H$, a series of geometry optimization calculations that progressively couple the C–H bond were performed. The result of these linear transit calculations was the generation of a σ-complex intermediate $[Me_2Si(C_5Me_4)_2]W(\sigma$-$C_6H_6)$, as illustrated in Figures 19 and 20. However, although the calculations indicate that the σ-complex $[Me_2Si(C_5Me_4)_2]W(\sigma$-$C_6H_6)$ is the intermediate that results directly from the reductive coupling step, this species is calculated to be unstable with respect to the η^2-π-benzene complex $[Me_2Si(C_5Me_4)_2]W(\eta^2$-$\pi$-$C_6H_6)$, as illustrated in Figure 20. In view of this result, it is important to consider the possibility that the η^2-π-benzene adduct $[Me_2Si(C_5Me_4)_2]W$-(η^2-π-C_6H_6) and the phenyl hydride derivative $[Me_2Si(C_5Me_4)_2]W(Ph)H$ may interconvert directly without the intermediacy of the σ-complex. To address the feasibility of a direct pathway between $[Me_2Si(C_5Me_4)_2]W(\eta^2$-$\pi$-$C_6H_6)$ and $[Me_2Si(C_5Me_4)_2]W(Ph)H$, a series of geometry optimization calculations that result in the direct oxidative cleavage of the C–H bond of $[Me_2Si(C_5Me_4)_2]W(\eta^2$-$\pi$-$C_6H_6)$ were performed by progressively bringing one of the benzene hydrogen atoms attached to the carbon atoms involved in the π-interaction towards the tungsten center. These calculations clearly demonstrated that the transition state for the direct transformation of $[Me_2Si(C_5Me_4)_2]W(\eta^2$-$\pi$-$C_6H_6)$ to $[Me_2Si(C_5Me_4)_2]W(Ph)H$ is prohibitively high. In contrast, a much lower energy pathway

(42) In this regard, it is worth noting that even though the intramolecular and intermolecular KIEs probe the same transition state, they are not expected to be identical because the intramolecular KIE specifically probes *only* the oxidative cleavage step (because that is where the partitioning occurs), whereas the intermolecular isotope effect will also be influenced to a certain degree by the isotope effects on the rate constants for association and dissociation of benzene, since $k_{oa} = k_{oc}k_a/(k_{oc} + k_d)$. Furthermore, inter- and intramolecular kinetic isotope effects are not necessarily expected to be equal because factors other than zero point energy differences influence kinetic isotope effects. Specifically, the kinetic isotope effect is conventionally described in terms of a product of four factors, namely, KIE = SYM·MMI·EXC·ZPE (where SYM is the symmetry factor, MMI is the mass moment of inertia term, EXC is the excitation term, and ZPE is the zero point energy term), and although the SYM factor is the same for the inter- and intramolecular comparison, the other terms are not the same. In particular, the MMI term associated with the different masses and moments of inertia of C_6H_6 and C_6D_6 is 1.5, whereas this value is unity for the intramolecular $C_6H_3D_3$ comparison because only one type of benzene molecule is involved. The MMI factor is, however, mitigated by the EXE term, which approaches $(1/MMI)(\nu^\ddagger_H/\nu^\ddagger_D)$ at high temperature. In view of these additional and competing factors, intra- and intermolecular kinetic isotope effects for the same fundamental reaction are not expected to be identical. See, for example: Slaughter, L. M.; Wolczanski, P. T.; Klinckman, T. R.; Cundari, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7953−7975.
(43) $K = [[Me_2Si(C_5Me_4)_2]Mo(C_6H_2D_3)H]/[[Me_2Si(C_5Me_4)_2]Mo(C_6H_2D_2)D]$.
(44) The overall equilibrium constant for oxidative addition of benzene is a composite of binding and activation steps. However, since only one type of η^2-π-benzene complex exists in the intramolecular competition experiment, the intramolecular EIE corresponds directly to the activation steps, i.e. the interconversion of $[Me_2Si(C_5Me_4)_2]Mo(\eta^2$-$\pi$-$C_6H_6)$ and $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$.
(45) Hascall, T.; Rabinovich, D.; Murphy, V. J.; Beachy, M. D.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 11402−11417.
(46) For example, the W–H bond in Cp_2WH_2 (74.3 kcal mol^{-1}) is 12.9 kcal mol^{-1} stronger than the Mo–H bond in Cp_2MoH_2 (61.4 kcal mol^{-1}). See: Dias, A. R.; Martinho Simões, J. A. *Polyhedron* **1988**, *7*, 1531−1544.
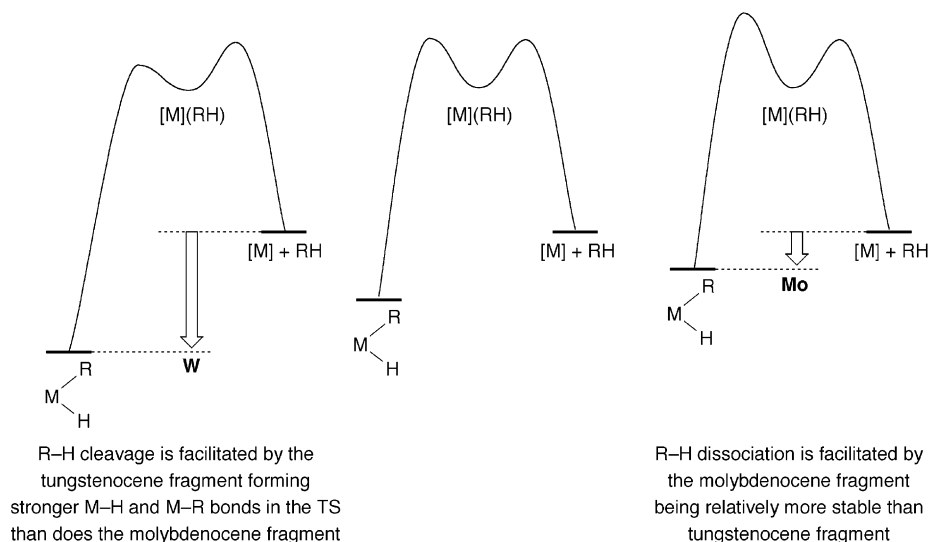
Figure 18. Rationalization of the different energy surfaces for Mo and W. The relative barriers for dissociation of R−H versus oxidative cleavage of a σ-complex are proposed to be influenced by the exothermicity of the overall transformation, with oxidative addition to tungsten being more exothermic than that to molybdenum.
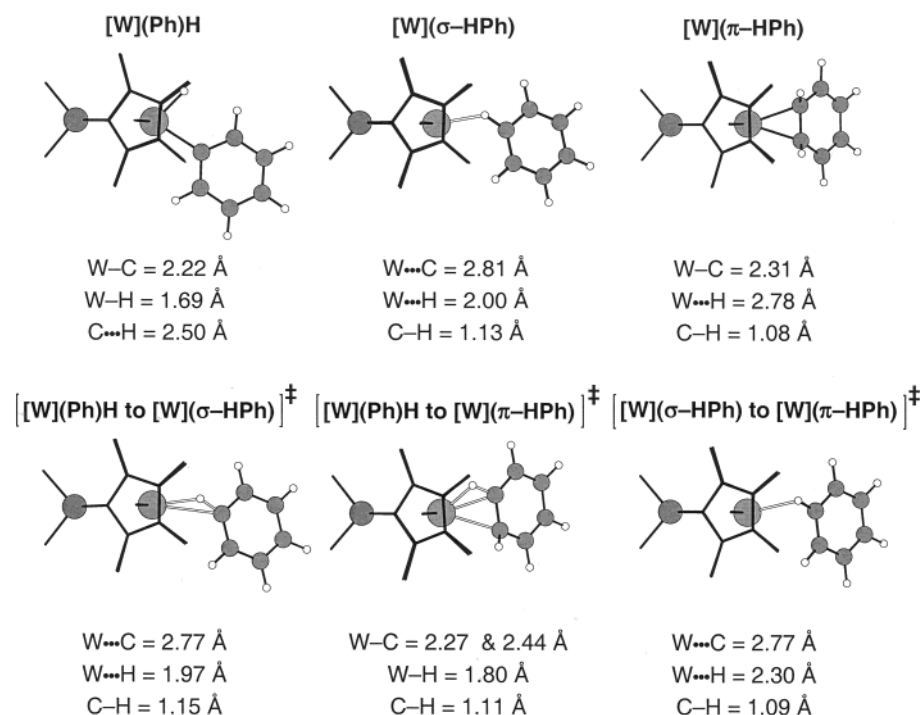

Figure 19. Geometry optimized structures of $[Me_2Si(C_5Me_4)_2]W(Ph)H$, $[Me_2Si(C_5Me_4)_2]W(\sigma\text{-HPh})$, and $[Me_2Si(C_5Me_4)_2]W(\eta^2\text{-}\pi\text{-}C_6H_6)$ and transition states for their interconversions (hydrogen atoms on methyl groups are omitted for clarity).

is calculated for a two-step sequence in which the $\eta^2\text{-}\pi$-benzene complex $[Me_2Si(C_5Me_4)_2]W(\eta^2\text{-}\pi\text{-}C_6H_6)$ first rearranges to the σ-complex $[Me_2Si(C_5Me_4)_2]W(\sigma\text{-}C_6H_6)$ and then undergoes subsequent oxidative cleavage of the C−H bond. The calculations, therefore, indicate that an $\eta^2\text{-}\pi$-benzene complex is *not* on the *direct* energy surface for reductive coupling and oxidative cleavage of benzene in this system.

Although the $\eta^2\text{-}\pi$-benzene intermediate is not on the direct energy surface for the oxidative cleavage and reductive coupling of the C−H bond, such a species may play an important role in the *overall* reductive elimination and oxidative addition process, as described by Jones and Perutz.[38] Specifically, since the η^2-π-benzene complex is thermodynamically more stable than the

σ-complex, it is possible that $\eta^2\text{-}\pi$-benzene coordination may provide a kinetically more favored interaction than that involving a σ-interaction. For such a situation, the overall oxidative addition of benzene to the metal center would proceed via a sequence involving initial $\eta^2\text{-}\pi$-benzene coordination, followed by isomerization to a σ-complex, and subsequent C−H oxidative cleavage. Correspondingly, microscopic reversibility dictates that reductive elimination would involve reductive coupling to give a σ-complex, isomerization to an $\eta^2\text{-}\pi$-benzene complex, followed by dissociation.

The notion that a benzene σ-complex may play an important role in oxidative addition and reductive elimination of aromatic C−H bonds has been previously considered.[39b,40,47] In particular,
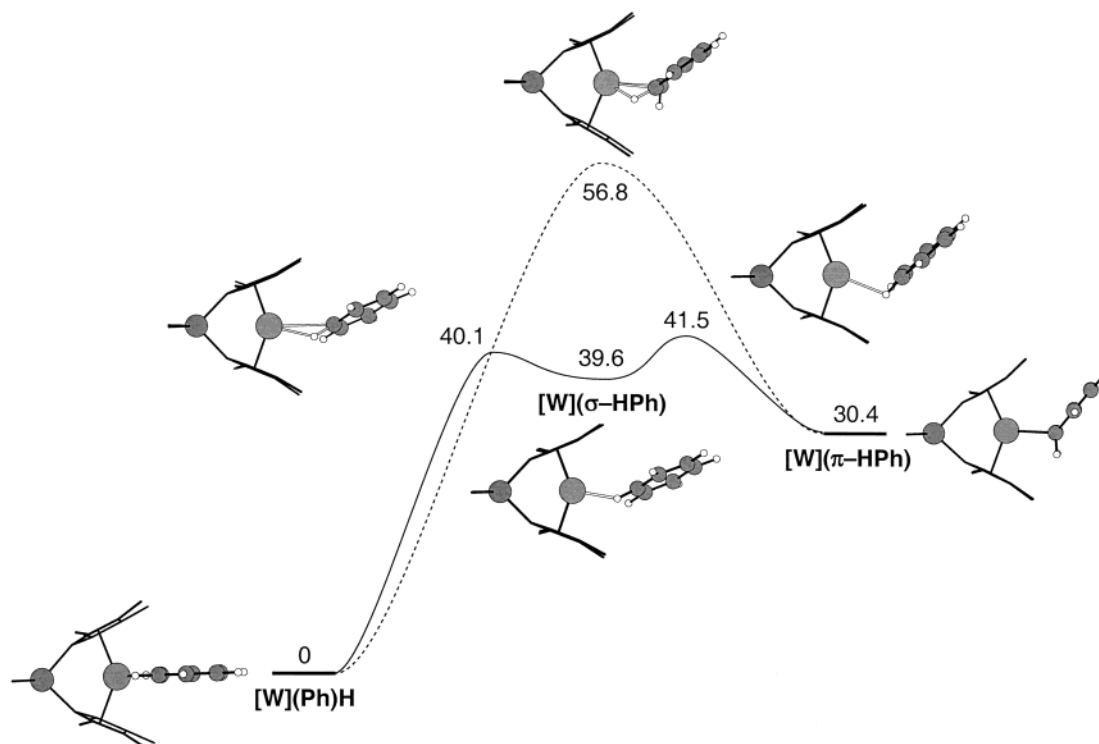
Figure 20. Calculated (B3LYP) energy surface for conversion of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H to [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) via [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-HPh). Energies are in kcal mol^{-1} and correspond to the enthalpies at 0 K, and are uncorrected for zero point energy.

Bercaw has stated that it is difficult to envision how an η^2-π-benzene complex could undergo direct C−H oxidative addition or conversely how the coupling of the C−H bond within a phenyl hydride complex would lead directly to an η^2-π-benzene species.[39b] For the present system, it is clear that steric interactions between the benzene ligand and the [Me$_2$Si(C$_5$Me$_4$)$_2$] ligand severely inhibit the direct oxidative cleavage of the C−H bond within the η^2-π-benzene complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$). Indeed, the structure of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) is strained by comparison to other η^2-π-benzene complexes because the cyclopentadienyl rings prevent the benzene ligand from coordinating in a perpendicular fashion to the tungsten center. For example, the W−(η^2-π-C$_6$H$_6$) hinge angle in [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) (127.1°) is substantially greater than the corresponding experimental values for {[η^2-Tp^{Me_2}]Pt(η^2-π-C$_6$H$_6$)H}{B[C$_6$H$_3$(CF$_3$)$_2$]$_4$} (106.2°)[39a] and TpRe(CO)(MeIm)(η^2-π-C$_6$H$_6$) (111.8°).[39c] Oxidative cleavage of the C−H bond in [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) naturally requires the tungsten center to approach the C−H bond which is prohibited by the orientation of the η^2-π-benzene ligand. In contrast, the orientation of the benzene in the σ-complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-C$_6$H$_6$) is much more suited to the cleavage of the C−H bond since the W−H interaction already exists, and a smooth transition to the phenyl hydride complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H is made possible.

Summary

In summary, the reductive elimination of RH from [Me$_2$Si(C$_5$Me$_4$)$_2$]M(R)H is characterized by an inverse KIE for the tungsten system, but a normal KIE for the molybdenum system.

(47) Lavin, M.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 99−104.

Oxidative addition of PhH to {[Me$_2$Si(C$_5$Me$_4$)$_2$]M} also differs for the two systems, with the molybdenum system exhibiting a substantial intermolecular KIE, while no effect is observed for the tungsten systems. These differences in KIEs for the molybdenum and tungsten systems indicate a significant difference in the reactivity of the hydrocarbon adducts [Me$_2$Si(C$_5$Me$_4$)$_2$]M(RH). Specifically, oxidative cleavage of [Me$_2$Si(C$_5$Me$_4$)$_2$]M(RH) is favored over RH dissociation for the tungsten system, whereas RH dissociation is favored for the molybdenum system. The origin of the difference between the molybdenum and tungsten systems is rationalized in terms of the difference in energies of the [Me$_2$Si(C$_5$Me$_4$)$_2$]M(R)H and {[Me$_2$Si(C$_5$Me$_4$)$_2$]M} species, which is greater for tungsten due to the stronger W−X versus Mo−X bonds. Stabilization of {[Me$_2$Si(C$_5$Me$_4$)$_2$]M} would be expected to reduce the barrier for dissociation of RH from [Me$_2$Si(C$_5$Me$_4$)$_2$]M(RH), with the result that the transition state for C−H oxidative cleavage becomes the highest point on the energy surface.

In addition to the KIEs, evidence for the methane σ-complex intermediate [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-HMe) is provided by the observation of H/D exchange between the hydride and alkyl sites of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D prior to reductive elimination of methane. Furthermore, a kinetics analysis of the interconversion of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_3$)D and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(CH$_2$D)H, with competitive elimination of methane, provides evidence that the reductive coupling step in this system is characterized by a normal KIE. This observation demonstrates that the inverse KIE for overall reductive elimination is the result of an inverse *equilibrium* isotope effect between [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Me)X and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-XMe) (X = H, D) and is *not* the result of an inverse KIE for a single step. In this regard, the previous report of an inverse kinetic isotope effect

of 0.76 for C−H reductive coupling in the [Tp]Pt(CH$_3$)H$_2$ system has been shown to be erroneous.

Finally, a computational study provides evidence that the reductive coupling of [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H proceeds via the initial formation of a benzene σ-complex, rather than an η^2-π-benzene complex, even though the latter species is more stable.

Experimental Section

The syntheses and characterization of all the compounds used in this study and the techniques used to measure kinetic and equilibrium isotope effects are described in the Supporting Information.

Computational Details

All calculations were carried out using DFT as implemented in the Jaguar 4.1 suite of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP functional and the 6-31G** basis set for C, H, and Si, while the transition metals were represented using the Los Alamos LACVP** basis set that includes relativistic effective core potentials. The energies of the optimized structures were reevaluated by additional single point calculations on each optimized geometry using the cc-pVTZ(-f) basis set that includes a double set of polarization functions. A modified version of LACVP**, designated as LACV3P**, was used for silicon and the transition metals.

The nature of the intermediate for the reductive coupling of the phenyl hydride complexes [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H was determined by performing a series of geometry optimizations as a function of the C···H separation. The result of these calculations was the generation of the σ-complex intermediate [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-HPh) that could be freely geometry optimized. The geometry of the transition state was refined by a quadratic synchronous transit (QST) calculation. The role of the η^2-π-benzene complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) on the energy surface was evaluated by two sets of linear transit scans: (i) to address the feasibility of the interconversion of the benzene η^2-π-complex and σ-complex, a series of geometry optimization calculations that progressively increase the W···C distance for one of the carbon atoms were performed, thereby resulting in the transformation to the σ-complex intermediate [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-HPh), as illustrated in Figure 20; (ii) to address the feasibility of a direct pathway between [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) and [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H, a series of geometry optimization calculations that progressively decrease the W···H distance were performed, thereby resulting in the transformation to the phenyl hydride, as illustrated in Figure 20. These calculations clearly demonstrate that the pathway for the direct transformation of Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) to [Me$_2$Si(C$_5$Me$_4$)$_2$]W(Ph)H is prohibitively high in energy compared to the two-step sequence in which the η^2-π-benzene complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W(η^2-π-C$_6$H$_6$) first isomerizes to the σ-complex [Me$_2$Si(C$_5$Me$_4$)$_2$]W(σ-C$_6$H$_6$).

Supporting Information Available: Experimental details (PDF) and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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