

Chapter 5

Kinetic and Equilibrium Deuterium Isotope Effects for C–H Bond Reductive Elimination and Oxidative Addition Reactions Involving the *Ansa*–Tungstenocene Methyl–Hydride Complex [Me₂Si(C₅Me₄)₂]W(Me)H

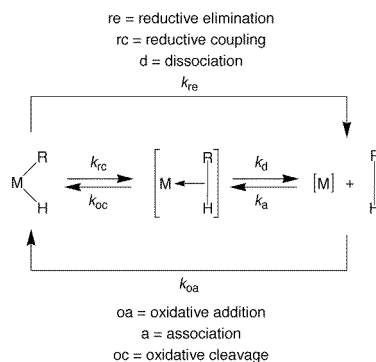
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The reductive elimination of methane from [Me₂Si(C₅Me₄)₂]W(CH₃)H and [Me₂Si(C₅Me₄)₂]W(CD₃)D is characterized by an inverse kinetic isotope effect (KIE). A kinetics analysis of the interconversion of [Me₂Si(C₅Me₄)₂]W(CH₃)D and [Me₂Si(C₅Me₄)₂]W(CH₂D)H, accompanied by elimination of methane, provides evidence that the reductive coupling step in this system is characterized by a normal KIE and that the inverse KIE for overall reductive elimination is a result of an inverse *equilibrium* isotope effect (EIE), rather than being a result of an inverse KIE for a single step. Calculations on [H₂Si(C₅H₄)₂]W(Me)H support these results and further demonstrate that the interconversion between [H₂Si(C₅H₄)₂]W(Me)H and the σ -complex [H₂Si(C₅H₄)₂]W(σ -HMe) is characterized by normal kinetic isotope effects for both reductive coupling and oxidative cleavage. Interestingly, the temperature dependencies of EIEs for coordination and oxidative addition of methane to the tungstenocene fragment {[H₂Si(C₅H₄)₂]W} are calculated to be very different, with the EIE for coordination approaching zero at 0K, while the EIE for oxidative addition approaches infinity.

Introduction

The oxidative addition and reductive elimination of C–H bonds at a transition metal center are reactions that are crucial to the functionalization of hydrocarbons.¹ An important component of these transformations is that they are mediated by σ -complexes, $[M](\sigma\text{-HR})$, in which the hydrocarbon is coordinated to the metal by 3-center-2-electron $M\cdots H-C$ interactions.^{2,3,4} Evidence for the existence of these σ -complexes includes: (i) low temperature spectroscopic and room temperature flash kinetics studies,^{3,5} (ii) the observation of deuterium exchange between hydride and alkyl sites, *e.g.* $[M](CH_3)D \rightarrow [M](CH_2D)H$, and (iii) the measurement of kinetic isotope effects (KIEs).⁶ As a result of the existence of σ -complex intermediates, the terms “reductive elimination” (re) and “oxidative addition” (oa) do not correspond to elementary steps and additional terms are required to describe adequately the overall mechanism. Thus, 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), as illustrated in Scheme 1.



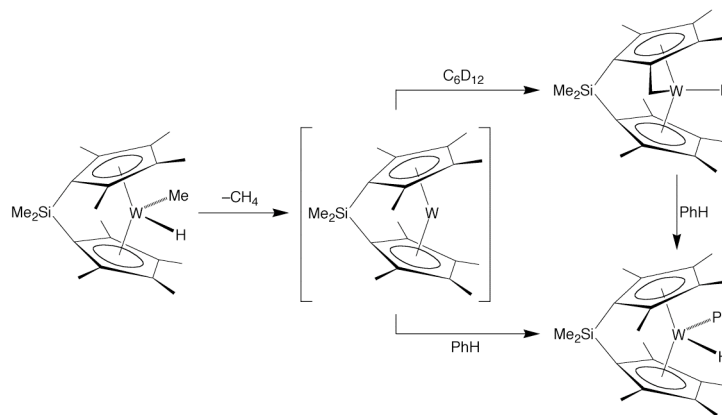
Scheme 1. Oxidative addition and reductive elimination mediated by σ -complex intermediates.

The present article describes experimental and computational studies designed to determine the kinetic and equilibrium isotope effects of the individual steps pertaining to oxidative addition and reductive elimination of methane involving the *ansa*-tungstenocene complex $[Me_2Si(C_5Me_4)_2]W(Me)H$.

Reductive Elimination of Methane from $[Me_2Si(C_5Me_4)_2]W(Me)H$

Previous studies have indicated that reductive elimination of methane from the tungstenocene methyl-hydride complexes $Cp_2W(Me)H$ ⁷ and $Cp^*W(Me)H$ ⁸ is

facile. The *ansa*-complex $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$ likewise reductively eliminates methane; the tungstenocene intermediate so generated is trapped intramolecularly to give $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^6\text{-C}_5\text{Me}_3\text{CH}_2)]\text{WH}$, or intermolecularly by benzene to give $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Ph})\text{H}$ (Scheme 2).⁹



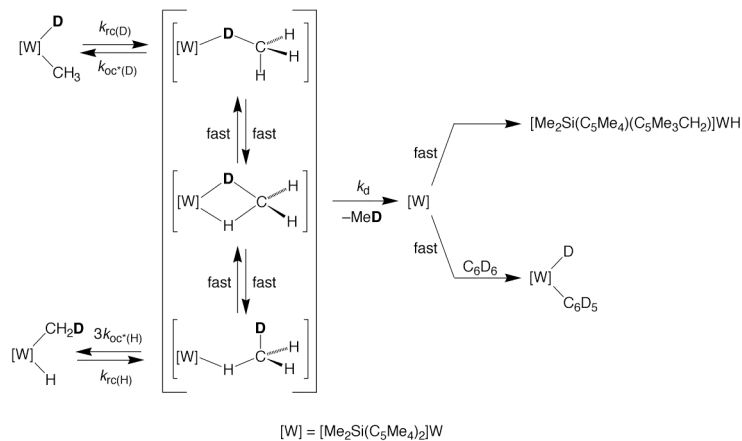
Scheme 2. Reductive elimination of methane from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$.

By comparison with $\text{Cp}^*_2\text{W}(\text{Me})\text{H}$, two noteworthy aspects of the reductive elimination of methane from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$ are: (i) the *ansa* bridge substantially inhibits the reductive elimination of methane, with $k_{\text{ansa}}/k_{\text{Cp}^*} = 0.03$ at 100°C ;¹⁰ and (ii) the *ansa* bridge promotes intermolecular C–H bond activation, with $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}\}$ being capable of being trapped by benzene to give the phenyl–hydride complex $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Ph})\text{H}$, whereas reductive elimination of methane from $\text{Cp}^*_2\text{W}(\text{Me})\text{H}$ in benzene gives only the tuck-in complex $\text{Cp}^*(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{WH}$. Kinetics studies, however, indicate that although intermolecular oxidative addition of benzene is thermodynamically favored, intramolecular C–H bond cleavage within $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}\}$ to give $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^6\text{-C}_5\text{Me}_3\text{CH}_2)]\text{WH}$ is actually kinetically favored.

Evidence for σ -Complex Intermediates: Kinetic Isotope Effects and Isotope Scrambling for $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{H}$ and its Isotopologues

Evidence that reductive elimination of methane from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$ proceeds via a σ -complex intermediate is provided by the observation of H/D exchange between the hydride and methyl sites of the isotopologue $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{D}$ resulting in the formation of $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_2\text{D})\text{H}$ (Scheme 3). Examples of such isotope exchange reactions are well known,⁶ and are postulated to occur by a sequence that

involves: (i) reductive coupling to form a σ -complex intermediate, (ii) H/D exchange within the σ -complex, and (iii) oxidative cleavage to generate the isotopomeric methyl-hydride complex (Scheme 3).



Scheme 3. H/D Exchange via a σ -complex intermediate.

Further evidence for the existence of a σ -complex intermediate in the reductive elimination of methane is obtained from the observation of an *inverse* (*i.e.* < 1) kinetic isotope effect of 0.45(3) for reductive elimination of CH_4 and CD_4 from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{H}$ and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CD}_3)\text{D}$ at 100°C . Specifically, the rate constant for reductive elimination is a composite of the rate constants for reductive coupling (k_{rc}), oxidative cleavage (k_{oc}), and dissociation (k_{d}), namely $k_{\text{obs}} = k_{\text{rc}}k_{\text{d}}/(k_{\text{oc}} + k_{\text{d}})$. For a limiting situation in which dissociation is rate determining (*i.e.* $k_{\text{d}} \ll k_{\text{oc}}$), the expression simplifies to $k_{\text{obs}} = k_{\text{rc}}k_{\text{d}}/k_{\text{oc}} = K_{\sigma}k_{\text{d}}$, where K_{σ} is the equilibrium constant for the conversion of $[\text{M}](\text{R})\text{H}$ to $[\text{M}](\sigma\text{-RH})$. As such, the kinetic isotope effect for overall reductive elimination is $k_{\text{H}}/k_{\text{D}} = [K_{\sigma(\text{H})}/K_{\sigma(\text{D})}][k_{\text{d}(\text{H})}/k_{\text{d}(\text{D})}]$, where $K_{\sigma(\text{H})}/K_{\sigma(\text{D})}$ is the *equilibrium* isotope effect for the conversion of $[\text{M}](\text{R})\text{H}$ to $[\text{M}](\sigma\text{-RH})$ (Figure 1). If the isotope effect for dissociation of RH (*i.e.* $[k_{\text{d}(\text{H})}/k_{\text{d}(\text{D})}]$) is close to unity (since the C–H bond is close to being fully formed),^{6a} the isotope effect on reductive elimination would then be dominated by the *equilibrium* isotope effect $K_{\sigma(\text{H})}/K_{\sigma(\text{D})}$ for formation of the σ -complex $[\text{M}](\sigma\text{-RH})$. The latter would be predicted to be inverse on the basis of the simple notion that deuterium prefers to be located in the stronger bond, *i.e.* C–D versus M–D.¹¹ Consequently, an *inverse* KIE would be predicted for the overall reductive elimination, without requiring an inverse effect for a single step (Figure 1).¹² Indeed, this explanation has been used to rationalize the inverse KIEs for a variety of alkyl hydride complexes, including

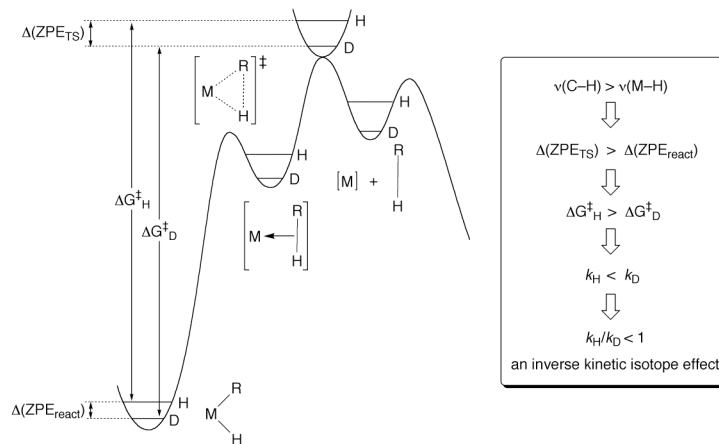


Figure 1. Origin of an inverse kinetic isotope effect for reductive elimination.

$\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_6\text{H}_{11})\text{H}$ (0.7),² $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C}_2\text{H}_5)\text{H}$ (0.5),^{12d} $\text{Cp}_2\text{W}(\text{Me})\text{H}$ (0.75),^{7b} $\text{Cp}^*_2\text{W}(\text{Me})\text{H}$ (0.70),⁸ $[\text{Cp}_2\text{Re}(\text{Me})\text{H}]^+$ (0.8),¹³ $[(\text{Me}_3\text{tacn})\text{Rh}(\text{PMe}_3)(\text{Me})\text{H}]^+$ (0.74),¹⁴ $(\text{tmeda})\text{Pt}(\text{Me})(\text{H})(\text{Cl})$ (0.29),¹⁵ $[\text{Tp}^{\text{Me}_2}]\text{Pt}(\text{Me})_2\text{H}$ (0.81), and $[\text{Tp}^{\text{Me}_2}]\text{Pt}(\text{Me})(\text{Ph})\text{H}$ (≤ 0.78).¹⁶

It must be emphasized that whereas an inverse KIE is to be expected if the σ -complex is formed prior to the rate determining step, a normal KIE would be expected if the reductive coupling step is rate determining since reactions which involve X–H(D) cleavage in the rate determining step are typically characterized by $k_{\text{H}}/k_{\text{D}}$ ratios greater than unity. Thus, for a limiting situation in which reductive coupling is rate determining (*i.e.* $k_{\text{d}} \gg k_{\text{oc}}$), the rate constant for reductive elimination simplifies to $k_{\text{obs}} = k_{\text{rc}}$. Since the transition state for reductive coupling involves cleavage of the M–H bond, $k_{\text{rc}(\text{H})}/k_{\text{rc}(\text{D})}$ might be expected to be > 1 and so a normal KIE would be expected for such a situation. Examples of complexes that exhibit normal KIEs include $(\text{Ph}_3\text{P})_2\text{Pt}(\text{Me})\text{H}$ (3.3),^{17a} $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2\text{CF}_3)\text{H}$ (2.2),^{17b} and $(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)\text{Pt}(\text{CH}_2\text{Bu}^t)\text{H}$ (1.5).^{17c}

While the preequilibrium explanation (Figure 1) has found common acceptance for the rationalization of inverse kinetic isotope effects for reductive elimination of RH, it must be emphasized that there is actually very little direct kinetic evidence to support it because the kinetic isotope effects for the individual steps are generally unknown. Rather, the common acceptance is in large part due to the fact that inverse primary *kinetic* deuterium isotope effects for a single step reaction are not well-known, while inverse *equilibrium* isotope effects for reactions that involve the transfer of hydrogen from a metal to carbon are certainly precedented.¹⁸ The question, therefore, arises as to whether it is possible that the inverse KIE for reductive elimination could actually be a result of an inverse kinetic isotope effect on reductive coupling. While it is not possible to address this issue by studying the kinetics of reductive elimination of

$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{H}$ and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CD}_3)\text{D}$, it is possible to address the issue by studying the elimination of CH_3D from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{D}$ and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_2\text{D})\text{H}$.⁹ Specifically, $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{D}$ is observed to isomerize to $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_2\text{D})\text{H}$ on a time-scale that is comparable to the overall reductive elimination of CH_3D , and a kinetics analysis of the transformations illustrated in Scheme 3 permits the KIE for reductive coupling to be determined. However, it must be emphasized that not all rate constants can be determined uniquely, and only relative values may be derived for reactions pertaining to the σ -complex intermediates (oxidative cleavage or dissociation) since they are not spectroscopically detectable. Thus, for the purpose of the analysis, the value for $k_{\text{oc}^*(\text{D})}$ was arbitrarily set as unity and rapid interconversion between the various σ -complex intermediates was assumed such that they were modeled by a single species $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3\text{D})\}$ with a single rate constant for the dissociation of methane (k_d). The simulation is illustrated in Figure 2, with the derived free energy surface presented in Figure 3. Significantly, a *normal* isotope effect of 1.4(2) is observed for $k_{\text{rc}(\text{H})}/k_{\text{rc}(\text{D})}$. Assuming that secondary effects do not play a dominant role in the reductive coupling of $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_2\text{D})\text{H}$, the value of 1.4(2) provides an estimate of the primary KIE for reductive coupling of $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{X}$ ($\text{X} = \text{H}, \text{D}$) to form the σ -complex intermediate $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\sigma\text{-XMe})$.

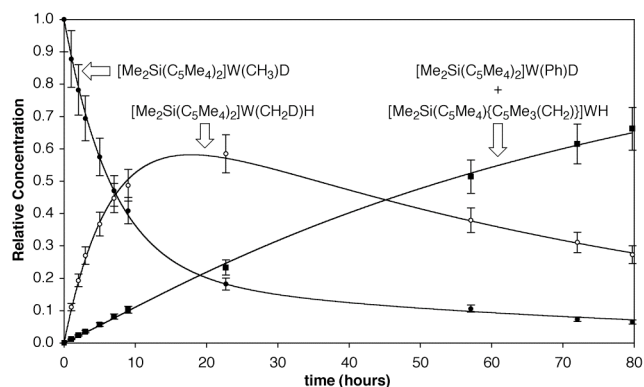


Figure 2. Kinetics simulation of isotope exchange within $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{D}$ and reductive elimination of methane.

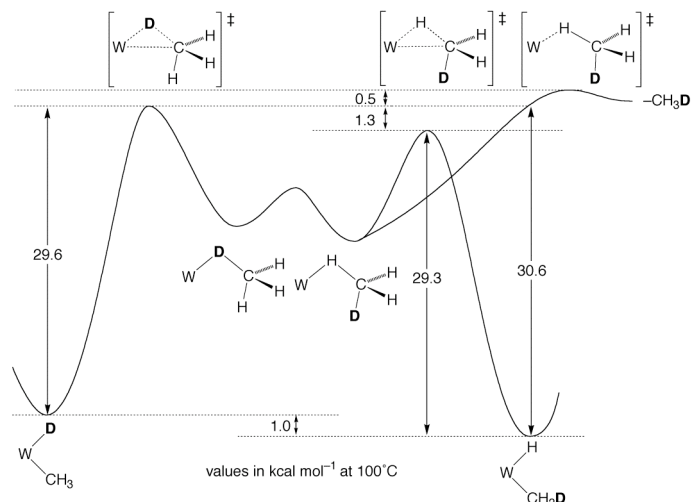


Figure 3. Free energy surface for interconversion of $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{D}$ and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_2\text{D})\text{H}$ and elimination of methane at 100°C. Note that for each pair of isotopomers, it is the one with deuterium attached to the carbon in a terminal fashion that is the lower in energy.

The observation of a normal kinetic isotope effect for reductive coupling within $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$ 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, in the most definitive study performed to date, has recently demonstrated that the EIE for the interconversion of $[\text{Tp}^{\text{Me}_2}]\text{Rh}(\text{L})(\text{Me})\text{X}$ and $[\text{Tp}^{\text{Me}_2}]\text{Rh}(\text{L})(\sigma\text{-XMe})$ is *inverse* (0.5), even though the individual KIEs for oxidative cleavage (4.3) and reductive coupling (2.1) are *normal* (L = CNCH_2Bu^t ; X = H, D).¹⁹

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 $[\text{Tp}]\text{Pt}(\text{Me})\text{H}_2$ is characterized by an *inverse* KIE of 0.76.²⁰ However, it has subsequently been recognized that the experiment performed is actually incapable of determining the KIE for reductive coupling unless the KIE for oxidative cleavage is known.^{6a,9} Furthermore, assigning the observed KIE to that for reductive coupling is only possible if the KIE for oxidative cleavage is unity. It is, therefore, evident that the experiment purported to determine an inverse kinetic isotope effect of 0.76 for the reductive coupling of $[\text{Tp}]\text{Pt}(\text{Me})\text{X}_2$ (X = H, D) has been erroneously interpreted, and that the system does not provide the claimed unprecedented opportunity to study the initial step of reductive coupling in alkyl hydride compounds.²¹

Computational Determination of Kinetic and Equilibrium Isotope Effects

In view of the experimental difficulty associated with determining the kinetic isotope effects for the individual steps comprising reductive elimination and oxidative addition, we have employed computational methods to determine these values for the reductive elimination of methane from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$.^{22,23} The mechanism for the reductive elimination reaction was determined by first performing a series of DFT (B3LYP) linear transit geometry optimizations that progressively couple the $\text{C}_{\text{Me}}\text{-H}$ bond. The result of these calculations was the generation of the σ -complex intermediate $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\sigma\text{-HMe})$ via a $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\sigma\text{-HMe})\}^\ddagger$ transition state (Figure 4).

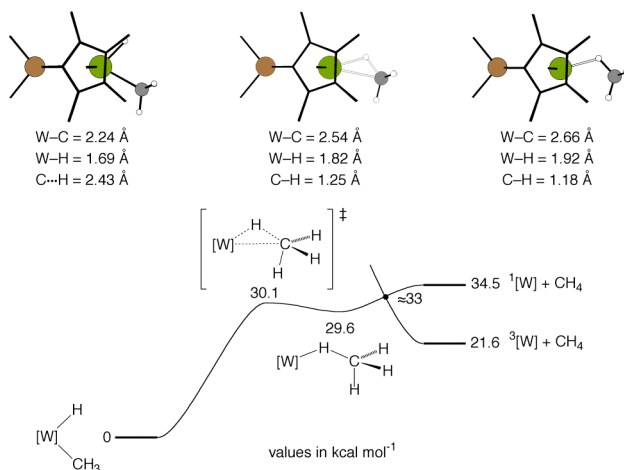


Figure 4. Calculated enthalpy surface for reductive elimination of CH_4 from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$.

Subsequent dissociation of methane from the σ -complex $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\sigma\text{-HMe})$ generates the 16-electron tungstenocene intermediate, $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}\}$. However, an important consideration relevant to the dissociation of methane from the σ -complex intermediate $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\sigma\text{-HMe})$ is that the parent tungstenocene $[\text{Cp}_2\text{W}]$ is known to be more stable as a triplet and thus dissociation of methane from singlet $\text{Cp}_2\text{W}(\sigma\text{-HMe})$ involves a spin crossover from the singlet to triplet manifold.^{23a,b} Likewise, triplet $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}\}$ is also calculated to be $12.9 \text{ kcal mol}^{-1}$ more stable than the singlet. The geometry of the crossing point for the singlet-triplet interconversion during dissociation of methane from

[Me₂Si(C₅Me₄)₂]W(σ-HMe) was estimated by using a procedure analogous to that used for [H₂C(C₅H₄)₂]W(σ-HMe).^{23a} Specifically, a series of geometry optimizations were performed on singlet [Me₂Si(C₅Me₄)₂]W(σ-HMe) in which the W...C_{Me} distance was progressively increased. At each point, the energy of the geometry optimized structure was determined in its triplet state, thereby allowing determination of the geometry for which the singlet and triplet states would be energetically degenerate.²⁴ The derived crossing point for [Me₂Si(C₅Me₄)₂]W(σ-HMe) is observed to occur with a W...C_{Me} distance of 3.3 Å, which is comparable to the value of 3.5 Å reported for [H₂C(C₅H₄)₂]W(σ-HMe).^{23b} The computed enthalpy surface for the overall reductive elimination is illustrated in Figure 4.

The computation of isotope effects requires knowledge of the vibrational frequencies of the participating species. However, since frequency calculations are highly computationally intensive, it was necessary to perform such studies on a computationally simpler system in which the methyl groups of the [Me₂Si(C₅Me₄)₂] ligand are replaced by hydrogen atoms, *i.e.* [H₂Si(C₅H₄)₂]W(Me)H. This simplification considerably facilitates the calculation, while still retaining the critical features of the molecules of interest.

Kinetic isotope effects are conventionally determined by the expression $KIE = k_H/k_D = SYM \cdot MMI \cdot EXC \cdot ZPE$ or a modification that employs the Teller-Redlich product rule $KIE = SYM \cdot VP \cdot EXC \cdot ZPE$.²⁵ In these expressions, SYM is the symmetry factor,^{26,27} MMI is the mass-moment of inertia term, EXC is the excitation term, ZPE is the zero point energy term, and VP is the vibrational product, as defined in Scheme 4.²⁸

$$SYM = \frac{\{(\sigma \nu \nu_H / (\sigma \nu \nu_D) \}}{\{(\sigma \nu \nu_H^\ddagger / (\sigma \nu \nu_D^\ddagger) \}} \quad MMI = \frac{(M_H^\ddagger / M_H)^{3/2} (I_H^\ddagger / I_H)^{1/2}}{(M_D^\ddagger / M_D)^{3/2} (I_D^\ddagger / I_D)^{1/2}} \quad VP = \prod (\nu_{iH}^\ddagger / \nu_{iD}^\ddagger) \prod (\nu_{iD} / \nu_{iH})$$

$$EXC = \frac{\prod \{ [1 - \exp(-u_{iH})] / [1 - \exp(-u_{iD})] \}}{\prod \{ [1 - \exp(-u_{iH}^\ddagger)] / [1 - \exp(-u_{iD}^\ddagger)] \}} \quad ZPE = \frac{\exp(\sum (u_{iH} - u_{iD}) / 2)}{\exp(\sum (u_{iH}^\ddagger - u_{iD}^\ddagger) / 2)}$$

Scheme 4. Definitions of SYM, MMI, VP, and ZPE.^{27,28}

The practical distinction between the two expressions is that the former requires the additional determination of the mass-moment of inertia term (MMI) for the structures of the molecules in question, while the latter requires determination of the vibrational product (VP) from the calculated frequencies. The two expressions should yield identical isotope effects given perfect data, but errors in computed frequencies may result in discrepancies.²⁹ Therefore, we not only calculated the isotope effects by both of these methods, but also determined the isotope effects by using the thermodynamic values obtained directly from the DFT calculations.³⁰ Significantly, the three methods yield very similar results, thereby providing an indication of the reliability of the calculations. In view of the similarity of the results obtained by the three methods, we present here only those derived from the expression, $KIE = SYM \cdot MMI \cdot EXC \cdot ZPE$, since this is the one that is more commonly featured in the literature.

Calculated primary and secondary KIE values for the individual transformations pertaining to the overall reductive elimination of methane from $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ are summarized in Table 1, illustrating several important points. Firstly, the primary KIE for reductive coupling of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{X}$ ($\text{X} = \text{H}, \text{D}$) to give the σ -complex $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-XMe})$ is small, but *normal* (1.05). Likewise, the microscopic reverse, *i.e.* oxidative cleavage of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-XMe})$, is also *normal* (1.60). The equilibrium isotope effect (EIE) for the interconversion of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{X}$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-XMe})$, however, is *inverse* (0.65), a consequence of the fact that the KIE for oxidative cleavage is greater than that for reductive coupling. Secondary isotope effects do not play a significant role, with values close to unity for the interconversion of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{CX}_3)\text{H}$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HCX}_3)$: $k_{\text{rc}(\text{H})}/k_{\text{rc}(\text{D})} = 1.02$, $k_{\text{oc}(\text{H})}/k_{\text{oc}(\text{D})} = 1.09$, and $K_{\sigma(\text{H})}/K_{\sigma(\text{D})} = 0.94$. Analysis of the individual SYM, MMI, EXC and ZPE terms indicates that it is the zero point energy term that effectively determines the magnitude of the isotope effects for the interconversion of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$ at 100 °C.

The KIE for dissociation of methane from a σ -complex has been postulated to be small.^{7b} Dissociation of methane from $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$ would likewise be expected to exhibit a small KIE, especially since the C–H bond in the σ -complex is almost fully formed ($d_{\text{C-H}} = 1.17 \text{ \AA}$). Despite the complication that the transition state for dissociation occurs at the singlet–triplet crossing point,³¹ frequency calculations on singlet $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$ with the geometry of the crossing point demonstrate that the KIEs for dissociation of methane are indeed close to unity (Table 1).

By predicting both a normal kinetic isotope effect for the reductive coupling step and an inverse kinetic isotope effect for the overall reductive elimination, the calculated isotope effects for reductive elimination of methane from $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ are in accord with the experimental study on $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{Me})\text{H}$. For example, the calculated inverse KIE for reductive elimination of methane from $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{CH}_3)\text{H}$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{CD}_3)\text{D}$ (0.58)³² compares favorably with the experimental value for $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{H}$ and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CD}_3)\text{D}$ (0.45). Analysis of the isotope effects for the various steps provides conclusive evidence that the principal factor responsible for the inverse nature of the KIE for the overall reductive elimination is the inverse *equilibrium* isotope effect for the interconversion of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$. The calculations therefore reinforce the notion that inverse primary kinetic isotope effects for reductive elimination of alkanes imply the existence of a σ -complex intermediate prior to rate determining loss of alkane. In addition to examining the kinetic isotope effects for loss of methane, it is instructive to evaluate the related equilibrium isotope effects. Interestingly, and in contrast to the negligible KIEs, the EIEs for dissociation of methane from the σ -complex [$K_{\text{d}(\text{H})}/K_{\text{d}(\text{D})}$] are large and inverse, as are those for complete reductive elimination [$K_{\text{H}}/K_{\text{D}}$] (Table 1).

Table 1. Primary (p) and secondary (s) isotope effects (IEs) pertaining to reductive elimination of methane from $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ at 100°C .^(a)

		SYM	MMI	EXC	ZPE	IE
$k_{\text{re}(\text{H})}/k_{\text{re}(\text{D})}$	p	1	1.000	1.047	0.999	1.047
	s	1	0.996	0.984	1.040	1.019
	p & s	1	0.996	1.035	1.003	1.035
$k_{\text{oc}(\text{H})}/k_{\text{oc}(\text{D})}$	p	1	1.006	1.033	1.538	1.599
	s	1	0.997	1.052	1.039	1.090
	p & s	1	1.003	1.077	1.597	1.725
$K_{\sigma(\text{H})}/K_{\sigma(\text{D})}$	p	1	0.994	1.014	0.650	0.654
	s	1	0.999	0.935	1.001	0.936
	p & s	1	0.993	0.961	0.628	0.600
$k_{\text{d}(\text{H})}/k_{\text{d}(\text{D})}$	p	1	1.003	0.898	0.975	0.879
	s	1	0.980	0.924	1.229	1.114
	p & s	1	0.983	0.852	1.148	0.962
$k_{\text{re}(\text{H})}/k_{\text{re}(\text{D})}$	p	1	0.997	0.911	0.633	0.575
	s	1	0.979	0.864	1.231	1.042
	p & s	1	0.976	0.819	0.721	0.577
$K_{\text{d}(\text{H})}/K_{\text{d}(\text{D})}$	p	0.25	0.688	1.139	0.944	0.185
	s	0.25	0.364	1.802	1.433	0.235
	p & s	1	0.276	2.003	1.246	0.689
$K_{\text{H}}/K_{\text{D}}$	p	0.25	0.684	1.155	0.613	0.121
	s	0.25	0.364	1.685	1.435	0.220
	p & s	1	0.274	1.925	0.783	0.413

(a) Primary effects (p) correspond to reductive elimination of $\text{CH}_3\text{-H}$ vs. $\text{CH}_3\text{-D}$; secondary effects (s) correspond to reductive elimination of $\text{CH}_3\text{-H}$ vs. $\text{CD}_3\text{-H}$; primary and secondary effects (p&s) correspond to reductive elimination of $\text{CH}_3\text{-H}$ vs. $\text{CD}_3\text{-D}$.

The inverse EIEs are a result of the SYM and MMI terms. Thus, the EIE for dissociation of methane from $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HCH}_3)$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-DCD}_3)$ is inverse due to the small value of the MMI term (0.28), a consequence of the fact that isotopic substitution has a substantial effect on the mass and moments of inertia of a molecule as small as methane. In addition to the MMI term, the SYM term also has a role in determining the EIE for dissociation of methane from $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HCH}_3)$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-DCH}_3)$ because the rotational symmetries of CH_3D and CH_4 are different.

An alternative perspective of the data presented in Table 1 is that the EIEs for both coordination (1.45) and oxidative addition (2.42) of methane to $\{[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}\}$ are normal, such that the reactions of CH_4 are thermodynamically more favored than those of CD_4 . To our knowledge, there are no experimental reports of the EIEs for coordination and oxidative addition of methane to a metal center,³³ although there are several conflicting reports of EIE's for coordination of other alkanes. Specifically, Geftakis and Ball reported a normal EIE (1.33 at -93°C) for coordination of cyclopentane to $[\text{CpRe}(\text{CO})_2]$,³⁴ whereas on the basis of kinetics measurements, Bergman and Moore reported substantially inverse EIEs for the coordination of cyclohexane (≈ 0.1 at -100°C) and neopentane (≈ 0.07 at -108°C) to $[\text{Cp}^*\text{Rh}(\text{CO})]$.³⁵

In view of these differing results, Bullock and Bender have commented that the issue of whether coordination of an alkane would be characterized by a normal or inverse EIE is not trivial.^{6b} Furthermore, Bender has calculated that the EIE for coordination of CH_4 and CD_4 to $\text{OsCl}_2(\text{PH}_3)_2$ giving *trans*-($\eta^2\text{-CH}_4$) $\text{OsCl}_2(\text{PH}_3)_2$ is almost unity at 27°C , but becomes inverse upon lowering the temperature, with a value of 0.66 at -108°C ; Bender has also noted that this change is not intuitively obvious.³⁶ Indeed, the inherent difficulty in predicting the EIE for coordination of an alkane is a consequence of the fact that isotopic substitution exerts different effects on the MMI, EXC, and ZPE terms, each of which have different temperature dependencies.

While Bender's calculations indicate that coordination of methane could be characterized by an inverse EIE, and thereby provide support for Bergman's studies on $[\text{Cp}^*\text{Rh}(\text{CO})]$,³⁵ they do not address the issue of how coordination of cyclopentane to $[\text{CpRe}(\text{CO})_2]$ could be characterized by a normal EIE. Specifically, because the EIE is unity at infinite temperature, it is not clear how a normal EIE could ever arise if EIE's only become more inverse upon reducing the temperature. Since we calculated a normal EIE for coordination of methane to $\{[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}\}$, we were intrigued to study its temperature dependence and determine whether it would become inverse upon lowering the temperature.

Most interestingly, rather than becoming inverse, the EIE at -100°C (1.57) actually *increased* slightly from the value at 100°C (1.45)! However, the relative insensitivity of the EIE with respect to temperature over this 200°C range is deceptive, as illustrated by the full temperature dependence illustrated in Figure 5. Thus, while the MMI term is temperature independent, the EXC and ZPE terms are strongly temperature dependent,³⁷ but with dependencies that oppose each other so that the product of EXC and ZPE does not vary markedly in the range -100°C to 100°C . Indeed, the EIE does not become inverse in this system until very low temperatures (*ca.* -200°C).³⁸

At *all* temperatures, the values of the ZPE and EXC terms are ≤ 1 and thereby favor an inverse EIE. However, these terms are mitigated by the large temperature independent MMI term (3.62) that dominates at temperatures \geq *ca.* -200°C . At low temperatures, the inverse EIE is a result of domination by the strongly inverse ZPE term. While the ZPE term is typically normal when the bond being broken is stronger than the one being formed,¹¹ the effect may become inverse when the reaction results in the creation of a species with a greater number of isotope sensitive vibrations,³⁹ as illustrated by the inverse

EIEs associated with the coordination and oxidative addition of H_2 to a metal center.⁴⁰ Since the ZPE term becomes zero at 0 K, the EIE likewise becomes zero.

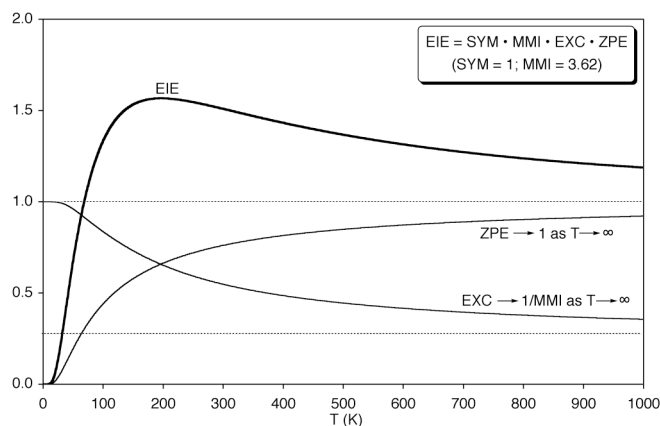


Figure 5. Calculated EIE as a function of temperature for coordination of methane to $\{[H_2Si(C_5H_4)_2]W\}$ as determined by the individual MMI, EXC, and ZPE terms.

At high temperatures, it is the EXC rather than ZPE term that becomes dominant in reducing the value of the EIE for coordination of methane. However, since EXC does not become zero at infinite temperature, but rather becomes $1/MMI$, the EXC term is incapable of causing the EIE to become inverse because the product $MMI \cdot EXC$ approaches unity.⁴¹

It is also instructive to analyze the temperature dependence of the EIE in terms of the combined $SYM \cdot MMI \cdot EXC$ term (which influences the entropy factor) and the ZPE term (which influences the enthalpy factor). Since EXC is unity at 0 K and is $1/MMI$ in the limit of infinite temperature, the product $MMI \cdot EXC$ varies from MMI to unity over this temperature range, as illustrated in Figure 6. Thus, at all temperatures the $SYM \cdot MMI \cdot EXC$ entropy factor favors a normal EIE, while the ZPE entropy factor favors an inverse EIE. At high temperatures $SYM \cdot MMI \cdot EXC$ dominates and the EIE is normal, while at low temperatures the ZPE term dominates and the EIE is inverse. If the form of the temperature dependence illustrated in Figures 5 and 6 applies to other systems, it is evident that it provides a means to rationalize *both* normal and inverse EIEs for alkane coordination. However, the precise form of the temperature dependence will depend critically on the structure of the σ -complex and its corresponding vibrational frequencies.

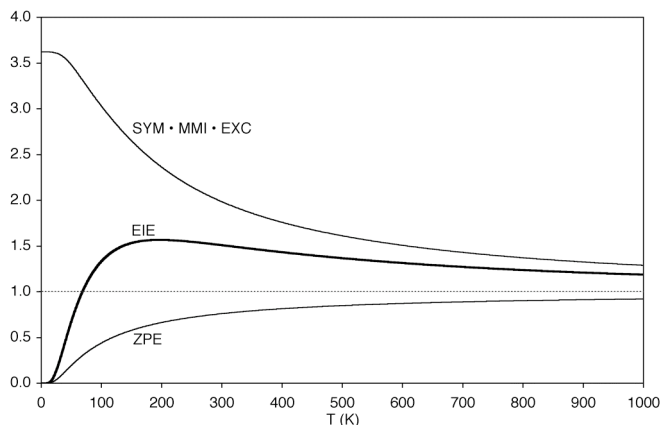


Figure 6. Calculated EIE for coordination of methane to $\{[H_2Si(C_5H_4)_2]W\}$ analyzed as a product of the combined $[SYM \cdot MMI \cdot EXC]$ and ZPE terms.

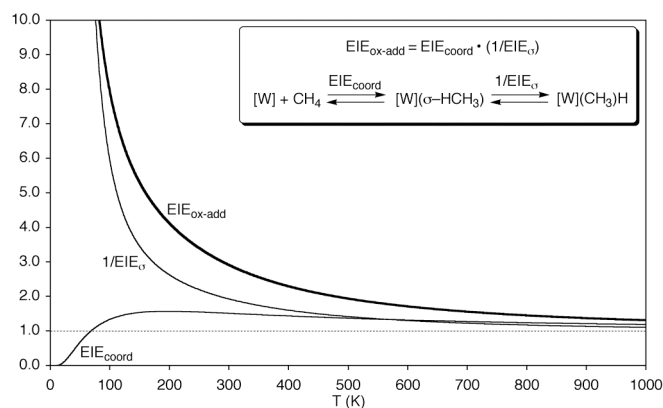


Figure 7. Markedly different temperature dependencies of the EIEs for coordination and oxidative addition of methane to $\{[H_2Si(C_5H_4)_2]W\}$.

Most interestingly, whereas the EIE for coordination of methane to $\{[H_2Si(C_5H_4)_2]W\}$ approaches zero at low temperature, the EIE for oxidative addition is normal at all temperatures and actually approaches infinity at 0K (Figure 7)!⁴² The dramatically different temperature dependencies of the EIEs for methane coordination and oxidative addition is associated with the ZPE terms: the ZPE term for coordination of methane is inverse at all temperatures (and zero at 0K), while the ZPE term for oxidative addition is normal at all

temperatures and approaches infinity at 0K. The ZPE term for coordination of methane is inverse because coordination results in the creation of additional isotope sensitive vibrations in the σ -complex $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$ that, in combination, are sufficiently strong to counter those associated with C–H bond in methane. In contrast, the isotopically sensitive vibrations associated with the W–H bond of the methyl hydride complex $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$, namely a W–H stretch and two bends, are of sufficiently low energy that they do not counter those associated with the C–H bond that has been broken. As a result, the ZPE term for oxidative addition of the C–H bond is *normal*. An alternative way of analyzing the situation is to recognize that the EIE for oxidative addition is a product of the EIEs for (i) methane coordination and (ii) oxidative cleavage of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$ to $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$, thereby demonstrating that it is the latter EIE_{oc} (*i.e.* $\text{EIE}_{\text{oc}} = 1/\text{EIE}_{\sigma} = 1/[K_{\sigma(\text{H})}/K_{\sigma(\text{D})}]$ in Table 1) which is dominant in determining the EIE for the overall oxidative addition. As indicated above, the normal EIE for the oxidative cleavage of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ is dictated by the σ -complex exhibiting the greater ZPE stabilization because the hydrogen is attached to carbon, rather than only to tungsten in $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$.

Summary

In summary, the reductive elimination of methane from $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CH}_3)\text{H}$ and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{W}(\text{CD}_3)\text{D}$ is characterized by an inverse KIE and calculations on $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ provide the first theoretical evidence that the origin of the inverse KIE is a manifestation of the existence of a σ -complex intermediate; thus, the inverse KIE is a consequence of an inverse equilibrium isotope effect for interconversion of $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\text{Me})\text{H}$ and $[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}(\sigma\text{-HMe})$, with KIEs for both reductive coupling and oxidative cleavage being normal. Interestingly, the temperature dependencies of EIEs for coordination and oxidative addition of methane to the tungstenocene fragment $\{[\text{H}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{W}\}$ are calculated to be very different, with the EIE for coordination approaching zero at 0K, while the EIE for oxidative addition approaches infinity.

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 32. As such, the derived transition state is not a well defined stationary point on the enthalpy surface; nevertheless, we have also calculated frequencies at other points on the singlet dissociation surface and find similar values.
 33. These calculations assume the preequilibrium approximation ($k_{oc} \gg k_d$) for reductive elimination (k_{re}), thereby corresponding to the most extreme inverse value for the system.
 34. 1,2-addition of CH₄ and CD₄ across the Ti=N bond of (Bu^t₃SiO)₂Ti=NSiBu^t₃ is, nevertheless, characterized by a normal EIE (2.00 at 26.5 °C). See: Slaughter, L. M.; Wolczanski, P. T.; Klinckman, T. R.; Cundari, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7953–7975.
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38. The ZPE term increases from zero to a limiting value of unity as the temperature is increased, while EXC decreases from unity to a limiting value of $1/MMI$ (*i.e.* $1/VP$).
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40. The additional vibrations are derived from rotational and translational degrees of freedom of the reactants.
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42. For any given set of vibrational frequencies, the product $VP \cdot EXC$ approaches unity at infinite temperature. Since VP is mathematically equivalent to MMI , the product $MMI \cdot EXC$ likewise approaches unity (as also required for the EIE to approach SYM). However, in view of the aforementioned errors in computed frequencies (reference 29), the calculated VP term may not be *exactly* equal to the MMI term. Thus while $VP \cdot EXC$ approaches unity, $MMI \cdot EXC$ actually approaches the ratio MMI/VP . For coordination and oxidative addition of methane to $\{[H_2Si(C_5H_4)_2]W\}$, the MMI/VP ratios are 1.05 and 1.01, respectively. These discrepancies have little effect on the derived EIE.
43. In this regard, it is worth noting that oxidative addition of CH_4 to $Ir(PH_3)_2(CO)H$ is also calculated to have a normal EIE of 3.64 at 300 K. See reference 40c.