Organometallics 1989, *8*, 1172–1179

Elimination Processes for Alkyl, Hydride, and Hydroxy Derivatives of Permethyltungstenocene†

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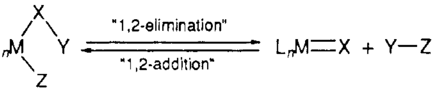
Received July 29, 1988

Elimination processes for alkyl, hydride, and hydroxy derivatives of permethyltungstenocene have been examined. The alkyl–hydride derivatives $Cp^*_2W(R)H$ ($Cp^* = \eta^5\text{-}C_5Me_5$; $R = CH_3$, $CH_2C_6H_5$) undergo facile intramolecular reductive elimination of R–H at 100 °C to give $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ with $k = 1.20\ (6) \times 10^{-4}$ and $1.13\ (6) \times 10^{-4}\ s^{-1}$, respectively. For $Cp^*_2W(CH_2C_6H_5)H$ the first-order rate constant has been measured as a function of temperature and the activation parameters, $\Delta H^\ddagger = 29.3\ (8)\ kcal{\cdot}mol^{-1}$ and $\Delta S^\ddagger = 1.5\ (2.0)$ eu, have been determined. The observation of (i) an inverse kinetic isotope effect for the elimination of methane from $Cp^*_2W(CH_3)H$ and $Cp^*_2W(CD_3)D$ ($k_H/k_D = 0.70\ (7)$ at 100 °C) and (ii) competitive incorporation of deuterium from the tungsten hydride position into the methyl ligand, i.e. $Cp^*_2W(CH_3)D \rightarrow Cp^*_2W(CH_2D)H$, provides evidence that the reductive elimination of the alkane proceeds via a "σ-complex" intermediate, $[Cp^*_2W(\eta^2\text{-}CH_4)]$. In contrast, facile reductive elimination is not observed for the dimethyl, dihydride, or hydroxy–hydride derivatives $Cp^*_2W(CH_3)_2$, $Cp^*_2WH_2$, or $Cp^*_2W(OH)H$, respectively. $Cp^*_2W(CH_3)_2$ eliminates 2 equiv of methane at 220 °C, forming $Cp^*\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2\}W$. The hydroxy–hydride derivative $Cp^*_2W(OH)H$ decomposes to a mixture of $Cp^*_2WH_2$, $Cp^*_2W{=}O$, and H_2O via initial disproportionation to $Cp^*_2WH_2$ and $[Cp^*_2W(OH)_2]$.

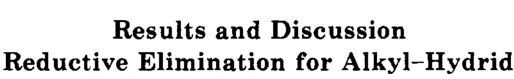
Introduction

Our research group had a long standing interest in the mechanisms of some of the fundamental transformations in organotransition-metal chemistry. Recent investigations of α and β migatory insertion and elimination reactions have focused on metallocene derivatives of the types $Cp'_2M({=}X)R$ (Cp′ = cyclopentadienyl or alkyl-substituted cyclopentadienyl; M = Nb, Ta; X = olefin or alkylidene, R = H or alkyl) and $Cp'_2ScCH_2CH_2R$. The convenient synthetic routes to these compounds, which allow systematic variations in R and X, and their high thermal stabilities and high solubilities have permitted quantitative measurements of the kinetics and thermodynamics for a variety of α and β migatory insertion and elimination processes.[1,2]

It occurred to us that the permethyltungstenocene system, with the ability of binding only two additional one-electron ligands, $Cp^*_2W(R)(R')$, or one two-electron ligand, $Cp^*_2W{=}X$, could be ideal for studying reductive elimination and 1,2-elimination[3] processes, i.e. eq 1 and 2. Here we describe studies designed to probe the nature of elimination reactions in the permethyltungstenocene system.



$$L_nM\begin{matrix}X\\Z\end{matrix} \underset{\text{"oxidative addition"}}{\overset{\text{"reductive elimination"}}{\rightleftharpoons}} [L_nM] + X{-}Z \qquad (1)$$



$$L_nM(X)(Z)Y \underset{\text{"1,2-addition"}}{\overset{\text{"1,2-elimination"}}{\rightleftharpoons}} L_nM{=}X + Y{-}Z \qquad (2)$$

Results and Discussion

1. Reductive Elimination for Alkyl–Hydride Derivatives. Alkyl–hydride derivatives are comparatively rare, and thus, there have been few mechanistic investigations into the nature of alkane elimination.[4] These studies have shown that intramolecular reductive elimination is not always the favored pathway for loss of alkane, and some systems undergo binuclear reductive elimination.

The elimination of methane from $Cp_2W(CH_3)H$ ($Cp = \eta^5\text{-}C_5H_5$) has been reported to occur via a combination of intramolecular reductive elimination and bimolecular pathways.[5] In view of the more sterically demanding nature of the Cp* versus Cp ligand, the intramolecular reductive elimination of alkanes from $Cp^*_2W(R)H$ is expected to dominate, thus providing a simpler system for mechanistic studies.

We have previously reported the syntheses and characterization of the alkyl–hydride derivatives $Cp^*_2W(CH_3)H$ and $Cp^*_2W(CH_2C_6H_5)H$.[6] Upon thermolysis (ca. 100 °C), these alkyl–hydride derivatives undergo a clean reductive elimination of the alkane (RH) with formation of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$.[6,7]

$$Cp^*_2W(R)H \rightarrow Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH + RH \qquad (3)$$

$$R = CH_3,\ CH_2C_6H_5$$

The final organotungsten compound presumably arises from attack at a C–H bond of one of the Cp* methyl groups of the initially formed $[Cp^*_2W]$. Unlike $Cp_2W(CH_3)H$, the bis(pentamethylcyclopentadienyl) system

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† Contribution no. 7708.

(1) For example, these studies have shown that (i) α-H migratory insertion to a methylidene ligand is favored by a factor of ca. 10^{10} over that of α-CH_3, (ii) α-H migratory insertion to methylidene is favored over that of β-H migratory insertion to olefin, and (iii) for one particular alkyl derivative, $[Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2CH_2CH_2)TaH]$, the rate of α-H elimination is ca. 10^8 that of β-H elimination, even though β-H elimination gives the more stable olefin–hydride product. Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21–39.

(2) (a) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347–5349. (b) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134–3146. (c) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976–978. (d) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E., manuscript in preparation.

(3) The term 1,2-elimination is not necessarily intended to imply a concerted reaction but only to indicate the overall transformation shown in eq 2.

(4) See, for example: (a) Norton, J. R. *Acc. Chem. Res.* **1979**, 139–145. (b) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–338. (c) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221–226. (d) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113–120.

(5) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727–729.

(6) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053–2082.

(7) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, 945–946.

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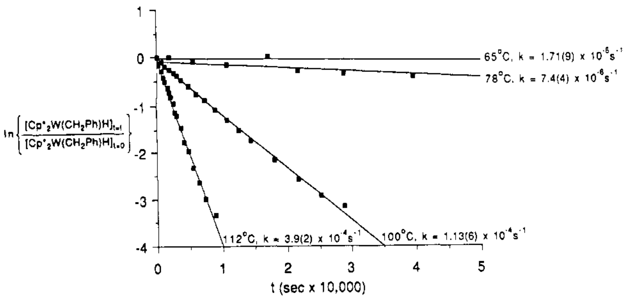

Figure 1.

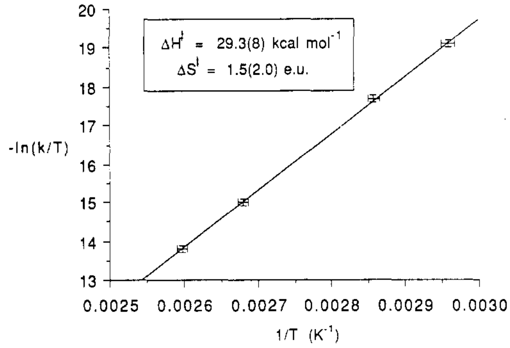

Figure 2.

provides its own intramolecular trap and, thus, does not require the addition of a trapping substrate (in that case, CD_3CN), simplifying the mechanistic scheme.

(i) Isotopic Labeling Studies. Isotopic labeling studies have been carried out to determine the molecularity of the reductive elimination and to establish whether or not pentamethylcyclopentadienyl ligand C–H bonds are participating, as has been observed for the zirconium derivative $Cp^*_2Zr(CH_2CHMe_2)H$.[8] Evidence that the hydrogen atom which couples with the methyl ligand to eliminate methane is, in fact, the W–H ligand is provided by the observation that elimination of methane from the d_4 derivative $Cp^*_2W(CD_3)D$ gives the isotopomers CD_4 and $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$, as judged by ^1H NMR spectroscopy.

$$Cp^*_2W(CD_3)D \rightarrow Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH + CD_4 \quad (4)$$

Similarly, $Cp^*_2W(CH_3)D$ yields the isotopomers $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ and CH_3D.

$$Cp^*_2W(CH_3)D \rightarrow Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH + CH_3D \quad (5)$$

Furthermore, thermolysis of a mixture of $Cp^*_2W(CH_3)H$ and $Cp^*_2W(CD_3)D$ does not result in crossover; e.g. CH_3D is not observed as a product (^1H NMR spectroscopy), in support of an *intramolecular* reductive elimination of methane.

(ii) Activation Parameters and Kinetic Deuterium Isotope Effects. Further evidence for the intramolecular nature of the reductive elimination is provided by the cleanly first-order kinetics of these reactions.[9] First-order plots for the elimination of toluene from $Cp^*_2W(CH_2C_6H_5)H$ over the temperature range 65–112 °C are shown in Figure 1. From these data the activation parameters $\Delta H^\ddagger = 29.3\ (8)$ kcal·mol^{-1} and $\Delta S^\ddagger = 1.5\ (2.0)$ eu have been calculated from an Eyring plot (Figure 2). Curiously, the rate of elimination of methane at 100 °C ($k_{100\,°C} = 1.20\ (6) \times 10^{-4}\ s^{-1}$) for the methyl–hydride derivative $Cp^*_2W(CH_3)H$ is very similar to the rate for the elimination of toluene from $Cp^*_2W(CH_2C_6H_5)H$ ($k_{100\,°C} = 1.13\ (6) \times 10^{-4}\ s^{-1}$). Both are slower than for $Cp_2W(CH_3)H$[5] ($k_{Cp}/k_{Cp^*} \approx 15$ at 100 °C), presumably indicating the stabilizing effect of the Cp* vs Cp ligands on the ground-state W(IV) complexes relative to the W(II)-like transition state.

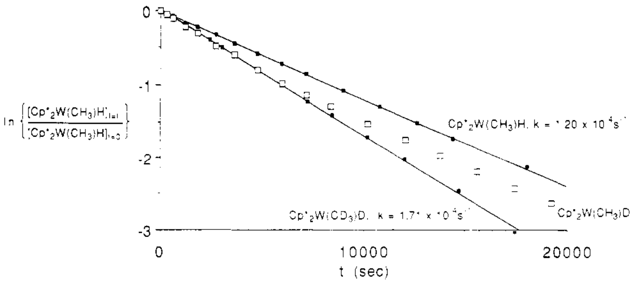

Figure 3.

The direction and magnitude of kinetic deuterium isotope effects were determined by comparing the decomposition rates for $Cp^*_2W(CH_3)H$, $Cp^*_2W(CH_3)D$, $Cp^*_2W(CD_3)H$, and $Cp^*_2W(CD_3)D$ (Figure 3). Significantly, the elimination of methane from the d_4 derivative $Cp^*_2W(CD_3)D$ occurs considerably *faster* than elimination from the d_0 derivative $Cp^*_2W(CH_3)H$. Thus, this reductive elimination reaction is characterized by an *inverse* (i.e. $k_H/k_D < 1$) primary kinetic deuterium isotope effect, $k_H/k_D = 0.70\ (7)$ at 100 °C.[10] An inverse kinetic deuterium isotope effect is also evident from the slower rate for the d_1 derivative $Cp^*_2W(CH_3)D$ ($k_H/k_D = 0.70\ (7)$).[11] The observation of an inverse kinetic deuterium isotope effect for reductive elimination of R–H versus R–D is intriguing, particularly in view of the normal k_H/k_D (i.e. $k_H/k_D > 1$) reported for the platinum alkyl–hydride derivatives $Pt(PPh_3)_2(CH_3)H$,[12] $Pt(PPh_3)_2(CH_2CF_3)H$,[13] and $Pt(Cy_2PCH_2CH_2PCy_2)(CH_2CMe_3)H$:[14] 3.3, 2.2, and 1.5, respectively.

Primary kinetic isotope effects have received considerable theoretical attention.[15] The simplest approximation for the calculation considers that the kinetic isotope effect arises only as a result of the zero point energy differences of the *reactant* isotopomers. This treatment assumes that the energy of the transition states will be the same for each

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(8) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966–5968.

(9) The concentrations of $Cp^*_2W(CH_2R)H$ used for examining the kinetics were typically 50–100 mM. The $[Cp_2W]$ system shows significant bimolecular reaction pathways at 14 mM and predominantly an intramolecular pathway at 0.67 mM (ref 5).

(10) Inverse secondary kinetic deuterium isotope effects are well-known and are normally interpreted as indicative of changes in hybridization strengthening the bonds which are not directly involved in the reaction. For this particular example, the net kinetic deuterium isotope effect is a composite of both primary and secondary effects; the secondary kinetic deuterium isotope effect would be expected to be negligible because the methyl group hybridization is sp^3 for both $Cp^*_2W(CH_3)H$ and CH_4. This assumption is supported by a $k_H/k_D = 1.0\ (1)$ measured for $Cp^*_2W(CH_3)D$ and $Cp^*_2W(CD_3)D$.

(11) For $Cp^*_2W(CH_3)D$, it is the *initial* rate of the reaction that is used in calculating this isotope effect. Since exchange of deuterium from the hydride to the methyl group to give $Cp^*_2W(CH_2D)H$ occurs on a similar time scale to reductive elimination (vide infra), nonlinear first-order kinetics are obtained, and the rate constant for the reaction decreases as the reaction progresses. The least-squares rate constant using all the data results in an inverse (but smaller) kinetic isotope effect ($k_H/k_D = 0.88$), nevertheless.

(12) (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916. (b) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–338. (c) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263–267.

(13) Michelin, R. A.; Faglia, S.; Uguagliati *Inorg. Chem.* **1983**, *22*, 1831–1834.

(14) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436–1448.

(15) (a) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980. (b) Bell, R. P. *Chem. Soc. Rev.* **1974**, *3*, 513–544.

isotopomer, since the vibration responsible for the zero point energy difference of the reactant isotopomers is no longer a vibration; rather it becomes the decomposition mode of the transition state. Therefore, this treatment predicts normal primary kinetic deuterium isotope effects with $k_H/k_D > 1$. A more complete treatment includes the structure of the transition state. Using this treatment, it has been concluded that, for a three-centered transition state, the kinetic deuterium isotope effect will be maximum for a symmetric transition state and will decrease for transition states which are either productlike or reactantlike.[16] In fact, for very unsymmetrical transition states, it has been predicted, both empirically[17] and theoretically,[16,18] that the kinetic deuterium isotope effect may become *inverse* for an elementary reaction in which the product possesses a very strong vibrational force constant compared to the reactant, and the transition state is productlike.[19]

On the other hand, an inverse primary kinetic deuterium isotope effect may also arise when the reaction proceeds stepwise, i.e. via an intermediate, prior to the rate-determining step. If the preequilibrium step generates an intermediate that possesses a larger difference in zero point energy relative to the reactant, then the overall kinetic deuterium isotope effect for the reaction may be inverse. In essence, the kinetic deuterium effect for the overall reaction will be a composite of a *thermodynamic* (equilibrium) isotope effect for the preequilibrium (with $K_H/K_D < 1$) and the kinetic deuterium isotope effect for the rate-determining step (which must be smaller than (K_H/K_D) in order for the net kinetic deuterium isotope effect to be <1). This situation will generally arise only if the preequilibrium involves transfer of H (or D) from an atom with which it vibrates at a low frequency to another atom with which it vibrates at a higher frequency (e.g. M–H to C–H). In effect, an inverse equilibrium isotope effect results in a greater preequilibrium concentration of the reactive intermediate for the deuterio isotopomer, compared with the protio isotopomer, and this increased concentration results in a faster rate for the overall reaction (so long as the new (e.g. the C–H) bond is not significantly altered in this rate-determining step).

Thus, an inverse kinetic deuterium isotope effect may, in theory, result from either (i) an elementary reaction in which the product possesses a very strong vibrational force constant compared to the reactant and the transition state is product-like or (ii) a stepise sequence involving transfer of a hydrogen (to an atom with which it vibrates at a higher frequency) prior to the rate-determining step. To our knowledge, however, there is no definitive experimental evidence for a single elementary step that exhibits an inverse primary kinetic isotope effect. Indeed, all inverse primary kinetic deuterium isotope effects that have been reported may be explained by the occurrence of a preequilibrium.

We have recently reported inverse kinetic isotope effects for reactions of $Cp^*_2Ta({=}CH_2)H$, and we interpreted these in terms of a preequilibrium involving α-H migratory insertion to give the intermediate $[Cp^*_2Ta{-}CH_3]$.[20] Although this intermediate cannot be observed directly by ^1H NMR spectroscopy, evidence for its existence comes from (i) trapping reactions to give $Cp^*_2Ta(CH_3)L$ and (ii) observation of magnetization transfer between the hydride and methylene protons. Significantly, although elimination of methane (via $[Cp^*_2TaCY_3]$) of $Cp^*_2Ta({=}CY_2)Y$ (Y = H, D) is faster for the deuterio isotopomer (k_H/k_D = 0.43 (1) at 80 °C), it was shown that for the closely analogous (chiral) derivative $Cp^*(\eta^5\text{-}C_5Me_4Ph)Ta({=}CH_2)H$, the elementary step ($k_1$) involving hydrogen migration to give the intermediate $[Cp^*(\eta^5\text{-}C_5Me_4Ph)Ta{-}CH_3]$ exhibited a *normal* kinetic isotope effect ($k_{1,H}/k_{1,D}$ = 2.0 (6) at 60 °C). Similarly, the inverse isotope effects that have been observed for other systems, such as transition-metal-catalyzed olefin hydrogenation reactions, may be interpreted in terms of a preequilibrium thermodynamic isotope effect.[21]

Bergman and co-workers have recently addressed the question of the origin of inverse kinetic deuterium isotope effects for the elimination of alkane from the alkyl–hydride derivatives $Cp^*Ir(PMe_3)(C_6H_{11})H$ (k_H/k_D = 0.7 (1) at 130 °C)[22] and $Cp^*Rh(PMe_3)(C_2H_5)H$ (k_H/k_D = 0.5 (1) at −30 °C).[23] They concluded that this effect is due to the formation of an intermediate in which a C–H bond has been formed. Evidence in favor of their mechanism, which *is independent* of the kinetic deuterium isotope effect, is the observation that the hydride ligand exchanges with the hydrogen atoms of the alkyl ligands prior to elimination of alkane. This intermediate, a "σ-complex", has a C–H σ-bond of the alkane coordinated to the metal center, similar to the bonding in alkyl derivatives having "agostic" M–H–C ligands.[24] These σ-complexes have been calculated to exist along the reaction profile for the oxidative addition of methane to unsaturated metal centers.[25] Although there are presently no well-characterized examples of alkane complexes of the transition metals, evidence for such complexes has been provided by both low-temperature matrix-isolation studies, e.g. $M(CO)_5(CH_4)$ (M = Cr, Mo, W)[26] and $Fe(CO)_4(CH_4)$,[27] and also for studies in solution at room temperature, $Cr(CO)_5(C_6H_{12})$.[28] Although

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[16] Bigeleisen, J. *Pure Appl. Chem.* **1964**, *8*, 217–223.

[17] (a) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295–306. (b) Creemers, H. M. J. C.; Verbeek, F.; Noltes, J. G. *J. Organomet. Chem.* **1967**, *8*, 469–477.

[18] Melander, L. *Acta. Chem. Scand.* **1971**, *25*, 3821–3826.

[19] It has also been predicted that inverse kinetic isotope effects may be observed for reactions in which the transition state are reactantlike if certain temperature-dependent terms outweigh temperature-independent terms (ref 16).

[20] Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21–39.

[21] (a) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119–1140. (b) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335–8337. (c) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299–311. (d) Sweany, R. L.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487–492. (e) Sweany, R.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57–63. (f) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575–584. (g) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1980**, *199*, 265–269. (h) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Mol. Catal.* **1982**, *16*, 43–49. (i) Roth, J. A.; Wiseman, P.; Ruzzala, L. *J. Organomet. Chem.* **1983**, *240*, 271–275. Although in some of the examples cited above the authors have interpreted inverse kinetic deuterium isotope effects as arising from preequilibrium, others have attributed them to a single step. We suggest that the latter examples may also be readily reinterpreted in terms of a preequilibrium.

[22] Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550.

[23] (a) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346. (b) Jones and Feher have also observed an inverse kinetic deuterium isotope effect for reductive elimination of benzene from $Cp^*Rh(PMe_3)(C_6H_5)H$; however, the proposed intermediate $[Cp^*Rh(PMe_3)(\eta^2\text{-}C_6H_6)]$ differs from the C–H adducts described above, in that a C=C double bond of benzene is proposed to be coordinated to rhodium: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819.

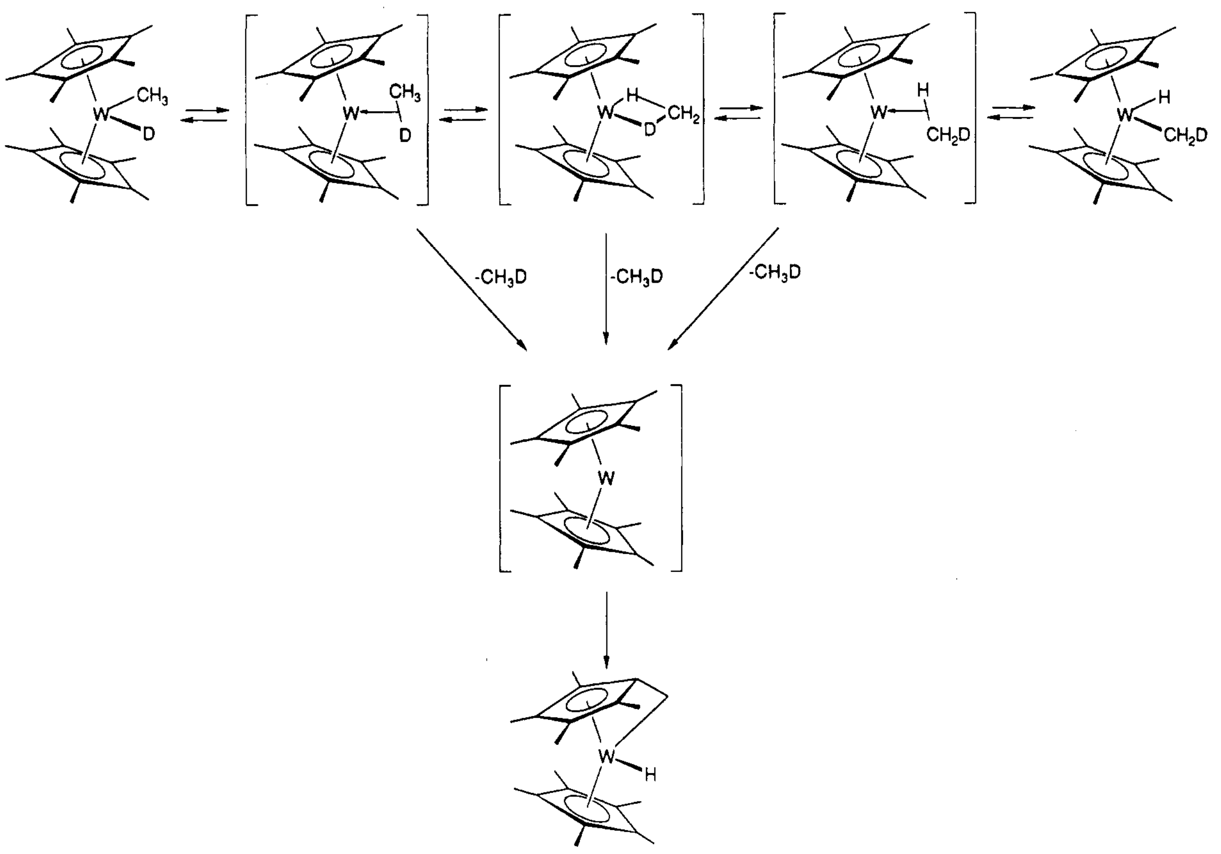
[24] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

[25] Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

[26] Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791–4808.

[27] Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276–2285.

Scheme I



the nature of the bonding interaction of the alkane with the metal center was not addressed for these species, it is likely that they are, in fact, also σ-complexes. The generic nature of these σ-complexes is accentuated by (i) the structural characterization of derivatives possessing both (η^2-Si–H) bonds, e.g. (η^6-C_6Me_6)$(CO)_2Cr(\eta^2$-H–$SiHPh_2$) and Cp*$(CO)_2Mn(\eta^2$-H–$SiHPh_2$),[29] and (η^2-B–H) bonds, i.e. a "side-on" bonded tetrahydridoborate derivative, $Ti(\eta^2$-H–$BH_3)_2(\eta^2$-$H_2BH_2)(PMe_3)_2$,[30] and (ii) the suggestion that species such as CH_5^+ may be more correctly formulated as dihydrogen derivatives, e.g. $CH_3(\eta^2$-$H_2)^+$.[31]

These σ-complexes are also analogues to the now familiar dihydrogen complexes.[32] In the present context, an inverse kinetic deuterium isotope effect has also been observed for a process involving reductive elimination of H_2 from $[Ir(PPh_3)_2(nbd)H_2]^+$ (nbd = norbornadiene),[33] which likely arises from the formation of a dihydrogen complex intermediate, $[Ir(PPh_3)_2(nbd)(\eta^2$-$H_2)]^+$.

In light of this growing body of evidence supporting the existence of such H–R σ-complexes (R = alkyl, H, Si, B), we propose that the inverse primary kinetic isotope effect for the elimination of CH_4 from $Cp^*_2W(CH_3)H$ is due to the presence of the intermediate, $[Cp^*_2W(\eta^2$-$CH_4)]$, which undergoes subsequent dissociation of methane from the permethyltungstenocene moiety (Scheme I). A mechanism involving $[Cp^*_2W(\eta^2$-$CH_4)]$ is further supported by the observation that deuterium is incorporated into the W–CH_3 group of the d_1 derivative $Cp^*_2W(CH_3)D$, giving $Cp^*_2W(CH_2D)H$ (Scheme I), prior to reductive elimination.[34]

$$Cp^*_2W(CH_3)D \rightleftarrows Cp^*_2W(CH_2D)H \qquad (6)$$

The exchange process (Scheme I) may proceed via a species which contains two bridging hydrogen atoms, $[Cp^*_2W((\mu$-$H)_2CH_2)]$ (cf. η^2-BH_4), e.g., eq 7. The rate of this

$$[Cp^*_2W(\eta^2\text{-D–}CH_3)] \rightleftarrows [Cp^*_2W((\mu\text{-D})(\mu\text{-H})CH_2)] \rightleftarrows [Cp^*_2W(\eta^2\text{-H–}CH_2D)] \qquad (7)$$

exchange process is, in fact, slightly slower than that for the overall elimination process. Thus, elimination of the alkane from the σ-complex, $[Cp^*_2W(\eta^2$-$CH_4)]$, is slightly favored over the isomerization process.

Consideration should be given to the possibility that the intermediate involved in this exchange process may not be the same as that on the reductive elimination pathway. For example, the hydrogen exchange between methyl and

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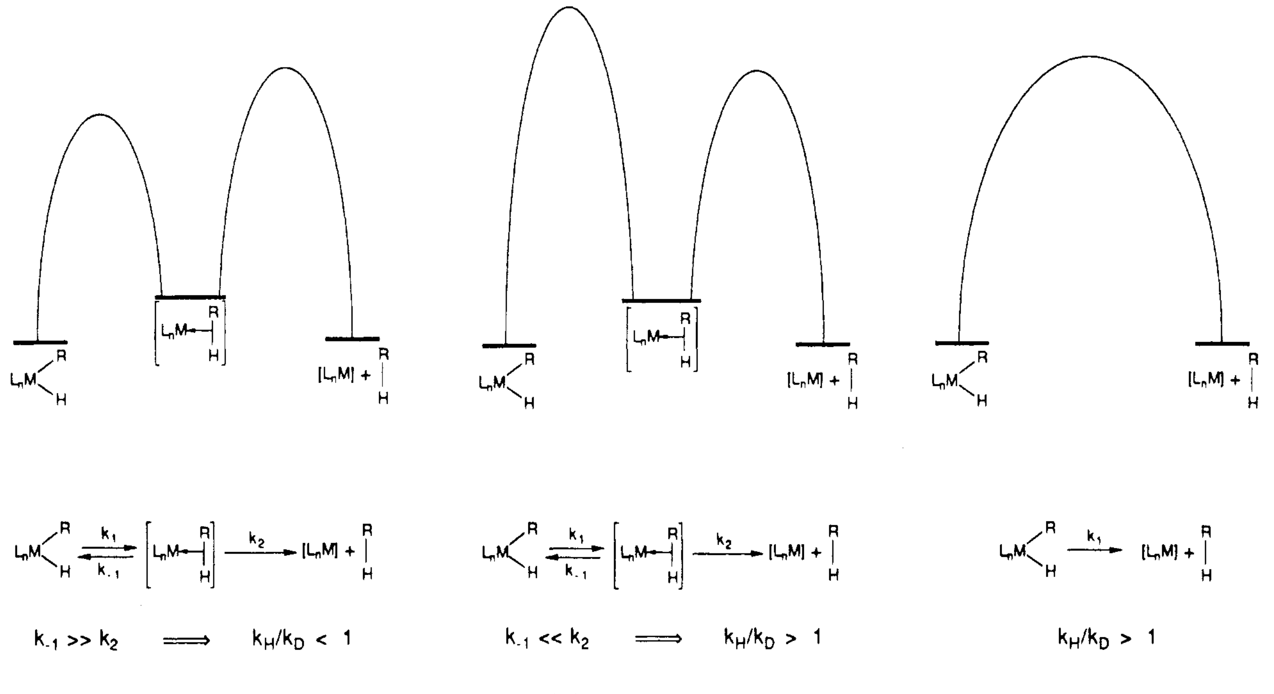
(34) A similar intramolecular exchange process between hydride and methyl groups has been observed for $Cp_2W(CH_3)H$ in dilute solutions (0.67 mM). In contrast, more concentrated (14.0 mM) solutions result in this exchange via an intermolecular process (ref 9). However, concentrated solutions of $Cp^*_2W(CH_3)D$ (ca. 70 mM) decompose giving predominantly CH_3D (ca. 93%) demonstrating that for the permethyltungstenocene system the exchange process is intramolecular.



Inverse Primary Kinetic Isotope Effect (a)

Normal Primary Kinetic Isotope Effect (b)

Normal Primary Kinetic Isotope Effect (c)

Figure 4.

hydride ligands could possibly obtain by an α-H elimination pathway involving $Cp^*(\eta^3\text{-}C_5Me_5)W(=CH_2)(H)(D)$.[35] Alternate pathways such as these cannot be unequivocally eliminated; however, we feel that it is most likely that the σ-complex is an intermediate common to both the hydrogen exchange and reductive elimination processes.

The exchange process is also manifested in the kinetics of the elimination of CH_3D from $Cp^*_2W(CH_3)D$. At the beginning of the reaction the rate constant is the same as that for the d_4 derivative $Cp^*_2W(CD_3)D$ as can be seen in Figure 3. However, as the reaction progresses and the exchange process results in the formation of $Cp^*_2W(CH_2D)H$, the rate constant for the reaction decreases and approaches that of the d_0 derivative $Cp^*_2W(CH_3)H$. This feature is evident from the curvature in the first-order plot for $Cp^*_2W(CH_3)D$.

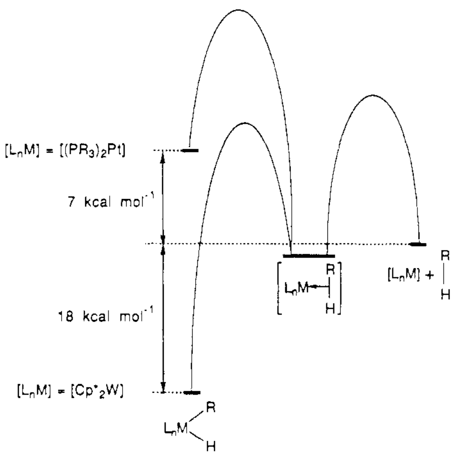


Figure 5.

(iii) Direction of Kinetic Deuterium Isotope Effects for Reductive Elimination of Alkane in Other Systems. Our observation and those of Bergman,[22,23] Norton,[36] and Heinekey[37] of *inverse* kinetic deuterium isotope effects for alkane reductive elimination stand in contrast to the *normal* kinetic deuterium isotope effects reported by Halpern,[12] Whitesides,[14] and Michelin.[13] This puzzling situation prompts the question of whether reductive elimination may follow two different mechanistic pathways: one mediated by a σ-complex and another, more conventional path not involving a σ-complex.[38] Consideration of the (hypothetical, thermoneutral) energy profiles for reductive elimination (Figure 4) reveals that *both* normal and inverse kinetic deuterium isotope effects could be observed when a σ-complex mediates loss of alkane—the characteristic feature is the energy of the transition state for dissociation of alkane relative to that of the transition state for σ-complex formation from the alkyl–hydride. As shown, an inverse kinetic deuterium isotope effect would result if $k_{-1} > k_2$ (Figure 4a), whereas if $k_{-1} < k_2$, a normal kinetic deuterium isotope effect would obtain (Figure 4b). The latter is not readily distinguished from a conventional reductive elimination pathway *not* mediated by a σ-complex (Figure 4c).

What factors determine whether a σ-complex comes before or after the highest transition state for elimination of alkane? Intriguingly, inverse kinetic deuterium isotope effects have been observed thus far only in systems where reductive elimination is thermodynamically quite unfavorable, i.e. only in systems where oxidative addition of the C–H bond of alkanes is facile. Normal kinetic deuterium isotope effects have been observed for those alkyl hydrides that are thermodynamically unstable. For example, using the best available bond dissociation energies

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(35) Elimination of methane from $Cp^*_2W(CH_3)H$ in the presence of D_2 occurs at the same rate and yields only CH_4, as in the absence. These results mitigate against a reversible 1,2-elimination pathway for $Cp^*_2W(CH_3)H$ to generate $Cp^*_2W{=}CH_2$ and H_2, as a means of achieving H/D exchange within $Cp^*_2W(CH_3)D$.

(36) Headford, C. E. L.; Kegley, S. E.; Bullock, R. M.; Hennessy, K. M.; Norton, J. R. *J. Am. Chem. Soc.*, in press.

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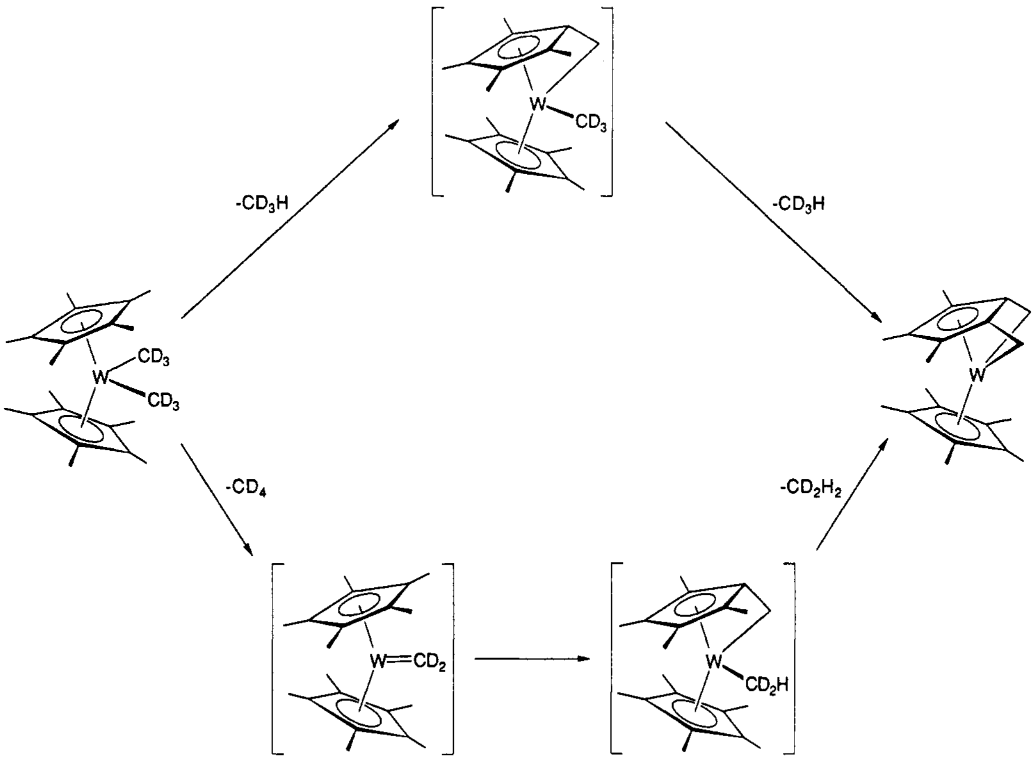
(38) Green has discussed these two possible pathways. See: Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897–1910.

Scheme II



[Ir–H = 75, Ir–CH_3 = 56; W–H = 73, W–CH_3 = 50, Pt–H = 58, Pt–CH_3 = 40, and CH_3–H = 105 kcal·mol^{-1}],[39] we may construct semiquantitative energy profiles for two endothermic reductive eliminations of methane (ΔH° = +26 kcal·mol^{-1} for Cp*Ir(PMe_3)(CH_3)(H) and ΔH° = +18 kcal·mol^{-1} for $Cp^*_2W(CH_3)(H)$) and an exothermic reductive elimination of methane (ΔH° = −7 kcal·mol^{-1} for $(PR_3)_2Pt(CH_3)(H)$) (Figure 5). We have made the assumption that the M–(C–H) bond dissociation energy for the σ-complex is small and comparable for each system. If we further assume that the activation energies for formation of the σ-complex from the methyl–hydride derivatives are not wildly different,[40] the instability of the methyl–hydride derivative of platinum (29 and 35 kcal·mol^{-1} higher than the tungsten and iridium derivatives, respectively) naturally leads to the σ-complex being positioned well below the transition state for its formation from the platinum system, whereas for the tungsten and iridium systems the barriers for regeneration of the methyl–hydride derivative from the σ-complex could reasonably be comparable (or less) than the barrier for dissociation of the C–H bond from the metal center. Thus, we suggest that the thermodynamics of the overall reductive elimination of alkane indirectly determine the relative transition-state energies from the σ-complex and, consequently, the direction of the kinetic deuterium isotope effect. Moreover, we suggest that these σ-complexes likely mediate all oxidative addition and reductive elimination reactions.

2. Elimination Processes for the Dimethyl, Dihydride, and Hydroxy–Hydride Derivatives $Cp^*_2W(CH_3)_2$, $Cp^*_2WH_2$, and $Cp^*_2W(OH)H$, Respectively. In contrast to the facile reductive elimination of R–H from $Cp^*_2W(R)H$ (R = CH_3, $CH_2C_6H_5$), the dimethyl derivative $Cp^*_2W(CH_3)_2$ is considerably more stable and does not afford ethane and $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$. In contrast, $Cp^*_2W(CH_3)_2$ eliminates only methane at 220 °C, and the final organometallic product is $Cp^*\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2\}W$.[7,41]

$$Cp^*_2W(CH_3)_2 \rightarrow Cp^*\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2\}W + 2CH_4 \quad (8)$$

Thus, for $Cp^*_2W(CH_3)_2$, reductive elimination is unfavorable relative to that for $Cp^*_2W(R)H$. The commonly invoked rationale is that the directional carbon sp^3 valence orbital, vis-à-vis the nondirectional hydrogen 1s valence orbital, results in less overlap and, hence, a higher transition state energy for ethane formation. Under forcing conditions, hydrogen abstraction occurs in preference, generating methane.

Two potential mechanisms (Scheme II) for this reaction involve (i) initial abstraction of the hydrogen atom of one of the W–CH_3 groups, analogous to the decomposition pathway followed by $Cp^*_2Ti(CH_3)_2$,[42] and (ii) initial abstraction of one of the hydrogen atoms of one of the Cp* methyl groups. In principle, analysis of the methane evolved from the d_6 derivative $Cp^*_2W(CD_3)_2$ could distinguish between these alternatives: a 1:1 mixture of CD_4 and CD_2H_2 for (i) and exclusively CD_3H for (ii). Unfortunately, at the temperatures required for methane evolution, extensive H/D exchange is observed, so that the methane generated includes considerable amounts of CH_4

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[39] (a) Stoutland, P. O.; Bergman, R. G. *Polyhedron*, in press. (b) Pilcher, G.; Skinner, H. A. *The Chemistry of the Metal-Carbon Bond*, Hartley, F. R. and Patai, S. Eds., Wiley: 1982; Vol. 1, pp 43–90. (c) Low, J. J.; Goddard, W. A. III *J. Am. Chem. Soc.* **1984**, *106*, 6928–6937. (d) Low, J. J.; Goddard, W. A. III *J. Am. Chem. Soc.* **1984**, *106*, 8321–8322. (e) Low, J. J.; Goddard, W. A. III *J. Am. Chem. Soc.* **1986**, *108*, 6115–6128. (f) Low, J. J.; Goddard, W. A. III *Organometallics* **1986**, *5*, 609–622.

[40] The range of activation energies for reductive elimination thus far reported are from $\Delta G^\ddagger$ = 18 kcal·mol^{-1} for $(PPh_3)_2Pt(H)(CH_3)$ (−25 °C; calculated from the reported rate constant) to $\Delta H^\ddagger$ = 36 kcal·mol^{-1} (160 °C) for Cp*Ir(PMe_3)(H)(C_6H_{11}).

[41] Some $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ (ca. 25%) is also formed, but it is not clear how this compound arises.

[42] McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629–1634.

and CH_3D. Thus, no conclusions may be reached regarding the mechanism for reaction 8.

The dihydride $Cp^*_2WH_2$ has previously been shown to *photochemically* eliminate H_2 and form sequentially $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ and $Cp^*\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2W\}$.[7] $Cp^*_2WH_2$ shows no evidence for *thermal* elimination of H_2; solutions of $Cp^*_2WH_2$ are stable even at 220 °C. This observation, per se, does not indicate that reductive elimination of dihydrogen is not occurring reversibly, since, in fact, $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ reacts with H_2 (140 °C, 1 day) to give $Cp^*_2WH_2$.[6]

$$Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH + H_2 \rightarrow Cp^*_2WH_2 \quad (9)$$

Heating $Cp^*_2WD_2$ (ca. >90% isotopically pure) in benzene-d_6 with H_2 (4 atm in a 5-mm NMR tube) at 140 °C for 2 weeks leads to an *increase* in the intensity of the $Cp^*_2WH_2$ resonance in the ^1H NMR spectrum, corresponding to approximately 40% $Cp^*_2WH_2$. However, when the intensity of the $W\text{-}H_2$ resonance in the ^1H NMR spectrum of the complementary system $Cp^*_2WH_2$ under D_2 (4 atm in a 5-mm NMR tube), *no* significant decrease is observed over a similar period. This apparently reduced rate is presumably due to scrambling of deuterium with the 30 hydrogens of the two pentamethylcyclopentadienyl ligands, thus greatly "diluting" the deuterium exchange into the W–H sites. These results argue for the (reversible) coupling of a hydride ligand with a hydrogen of a methyl group of a (η^5-C_5Me_5) ligand to afford $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ as a pathway for loss of H_2, perhaps the only pathway, since a reaction sequence involving reductive elimination followed by oxidative addition would result in comparable rates of exchange of hydrogen or deuterium into the W–H sites for the two complementary experiments described above. This coupling of a hydride ligand with a hydrogen of a methyl group of a (η^5-C_5Me_5) ligand is analogous to one of the proposed steps for loss of methane from $Cp^*_2W(CH_3)_2$.

Thus, whereas thermal reductive elimination is facile for the alkyl–hydride derivatives $Cp^*_2W(R)H$, both the dihydride, $Cp^*_2WH_2$, and dimethyl, $Cp^*_2W(CH_3)_2$, derivatives are considerably more stable and show much less tendency to reductively eliminate. This same trend is also evident from the decomposition temperatures reported for the tungstenocene analogues [$Cp_2W(CH_3)H$, ca. 60 °C; Cp_2WH_2, ca. 130 °C; $Cp_2W(CH_3)_2$, ca. 160 °C][43] and for the *cis*-$Os(CO)_4(R)(R')$ series [*cis*-$Os(CO)_4(CH_3)(H)$, ca. 50 °C; *cis*-$Os(CO)_4H_2$, 125 °C; *cis*-$Os(CO)_4(CH_3)_2$, ca. 160 °C].[44] For these, as well as the present examples in the permethyltungstenocene system, the most likely explanation is that the very high thermodynamic stability of the dihydride derivative dominates, whereas, as discussed above, the large kinetic barrier for loss of ethane from the dimethyl derivative dictates its thermal stability. The methyl–hydride compound is intermediate in both regards, and as a consequence, reductive elimination is more readily accessible.

For the hydroxy–hydride derivative $Cp^*_2W(OH)H$, pathways involving either reductive elimination or 1,2-elimination may operate. Other studies on the oxo derivatives $Cp^*_2W{=}O$ and $Cp^*_2Ta({=}O)H$ indicate that they react reversibly with H_2O and other substrates by a 1,2-addition/elimination process and that for the [$Cp^*_2Ta(OH)_2H$] intermediate, 1,2-elimination of H_2O is favored over reductive elimination of H_2O.[6] For $Cp^*_2W(OH)H$ reductive elimination of H_2O would give $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$, whereas 1,2-elimination of dihydrogen would give the oxo derivative $Cp^*_2W{=}O$. Interestingly, neither of these pathways appears to predominate, since thermolysis of $Cp^*_2W(OH)H$ at 80 °C gives equimolar quantities of $Cp^*_2W{=}O$ and $Cp^*_2WH_2$ with no evidence for $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$.

$$2Cp^*_2W(OH)H \rightarrow Cp^*_2W{=}O + Cp^*_2WH_2 + H_2O \quad (10)$$

The absence of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ demonstrates that reductive elimination of H_2O does not occur.[45] The formation of the equimolar mixture of $Cp^*_2W{=}O$ and $Cp^*_2WH_2$ may be rationalized by an intermolecular exchange process forming $Cp^*_2WH_2$ and [$Cp^*_2W(OH)_2$].

$$2Cp^*_2W(OH)H \rightleftarrows Cp^*_2WH_2 + [Cp^*_2W(OH)_2] \quad (11)$$

$$[Cp^*_2W(OH)_2] \rightarrow Cp^*_2W{=}O + H_2O \quad (12)$$

The exchange process shown in eq 11 is similar to that observed between $Cp^*_2WH_2$ and $Cp^*_2WCl_2$, which generates an equilibrium mixture with $Cp^*_2W(H)Cl$,[6] and the intermolecular exchange of hydride ligands of Cp_2WH_2 and $Cp_2W(H)(CH_3)$.[36] We have proposed the bis(hydroxide) derivative [$Cp^*_2W(OH)_2$] as an intermediate in the oxo exchange process of $Cp^*_2W{=}O$ with H_2O.[6] Thus, under these reaction conditions [$Cp^*_2W(OH)_2$] is expected to eliminate water and form $Cp^*_2W{=}O$, resulting in the observed stoichiometry: equimolar amounts of $Cp^*_2W{=}O$ and $Cp^*_2WH_2$.

Conclusions

These studies of elimination reactions of alkyl, hydride, and hydroxy derivatives of permethyltungstenocene demonstrate that the only facile reductive elimination pathway which operates is for the alkyl–hydride derivatives. The observation of both (i) an inverse kinetic isotope effect for the elimination of methane from $Cp^*_2W(CH_3)H$ and $Cp^*_2W(CD_3)D$ (k_H/k_D = 0.70 (7) at 100 °C) and (ii) the exchange of the hydride ligand with the hydrogen atoms of the methyl ligand, i.e. $Cp^*_2W(CH_3)D \rightarrow Cp^*_2W(CH_2D)H$, provides evidence that the reductive elimination of the alkane proceeds via a σ-complex intermediate. In the same way that dihydrogen complexes are considered to represent arrested forms of both oxidative addition and reductive elimination of dihydrogen, alkane σ-complexes may be considered to represent arrested forms of both oxidative addition and reductive elimination of alkane. The dimethyl derivative $Cp^*_2W(CH_3)_2$ does not reductively eliminate ethane but preferentially eliminates CH_4, possibly via a 1,2-elimination pathway. The thermal elimination of dihydrogen from $Cp^*_2WH_2$ appears to be highly unfavorable. Although the nature of the reaction(s) that lead to scrambling of hydrogen between the hydride ligands and free H_2 is presently uncertain, it appears that the direct coupling of the hydride ligand with one of the hydrogens of the methyl groups of the Cp* ligand is at least a competitive pathway. The hydroxy–hydride derivative undergoes neither reductive elimination of water nor 1,2-elimination of H_2. In preference an intermolecular exchange process occurs to generate equimolar quantities of $Cp^*_2WH_2$ and [$Cp^*_2W(OH)_2$], which rapidly undergoes an

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(44) Norton, J. R. *Acc. Chem. Res.* **1979**, 139–145.

(45) $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ does not react with 1 equiv of water below 80 °C.

intramolecular 1,2-elimination of water to form $Cp^*_2W{=}O$.

Experimental Section

All manipulations were performed by using glovebox, high-vacuum, or Schlenk techniques.[46] Solvents were purified and degassed by standard procedures. Benzene-d_6 was purified by vacuum transfer from activated molecular sieves (4 Å, Linde) and then from "titanocene".[47] ^1H, ^2H, ^{13}C, and ^{17}O NMR spectra were measured on Varian EM-390 (90 MHz) and JEOL GX400Q (400 MHz) spectrometers. General synthetic procedures and the syntheses of $Cp^*_2W(CH_3)H$, $Cp^*_2W(CH_2Ph)H$, $Cp^*_2WH_2$, $Cp^*_2W(CH_3)_2$, and $Cp^*_2W(OH)H$ are as described elsewhere.[6] The isotopomers (isotopic purity) $Cp^*_2W(CH_3)D$ (>95%), $Cp^*_2W(CD_3)H$ (>95%), $Cp^*_2W(CD_3)D$ (>95%), $Cp^*_2W(CD_3)_2$ (>95%), $Cp^*_2WD_2$ (>90%), and $Cp^*_2W(^{17}OH)H$ were synthesized by the appropriate isotopic substitution of the reagents.

Kinetic Measurements. Reactions were followed by monitoring the decrease in intensity of a selected resonance of the starting complex in solutions in benzene-d_6 (typically 50-100 mM) in a sealed NMR tube (CARE!). Reaction temperatures were maintained by using constant temperature baths and were observed to be constant to within ±1 °C. The NMR tubes were sealed containing >1 atm of dinitrogen. Total submersion in the bath prevented the benzene-d_6 from refluxing at elevated temperatures. Integrated intensities and peak heights were demonstrated to be reproducible to within ±7% by repeated measurement. Each spectrum was recorded 3 times and the average integrated intensity or peak height was used to calculate the values of k given in the text. $\Delta G^\ddagger(T)$ was calculated from the Eyring equation $\Delta G^\ddagger(T) = RT \ln (\kappa k_B T/kh)$, assuming a transmission coefficient, κ, of 1. Plots of $\ln (k/T)$ vs $1/T$ were constructed and yielded the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

Elimination of RH from $Cp^*_2W(R)H$ ($R = CH_3, CH_2C_6H_5$). Each experiment was conducted as described above to determine the rate constants for the elimination process at set temperatures. The product was characterized as $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ by comparison with the ^1H NMR data with that of an authentic sample.[6] For the elimination of methane from the various isotopomers of $Cp^*_2W(CH_3)H$, analysis of the products was measured by ^1H and ^2H NMR spectroscopy. Kinetic deuterium isotope effects were measured by comparing rates of the reactions carried out in separate experiments at 100 °C.

Elimination of Methane from a Mixture of $Cp^*_2W(CH_3)H$ and $Cp^*_2W(CD_3)D$. A solution of $Cp^*_2W(CH_3)H$ (25mg) and $Cp^*_2W(CD_3)D$ (25mg) in benzene-d_6 was heated at 100 °C. The products were examined by ^1H NMR spectroscopy, which demonstrated the absence of crossover products, e.g. CH_3D.

Elimination of CH_4 from $Cp^*_2W(CH_3)H$ in the Presence of D_2 or C_2H_4. Solutions of $Cp^*_2W(CH_3)H$ (50–100 mM) in benzene-d_6 were treated separately with C_2H_4 (ca. 10 equiv) and D_2 (4 atm). The reaction was monitored as described above, at 100 °C, and occurred with the same rate constant as in the absence of substrate, giving the same product $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$. Appropriate shielding precautions were taken when heating pressurized NMR tube samples.

Elimination of CH_4 from $Cp^*_2W(CH_3)_2$. A solution of $Cp^*_2W(CH_3)_2$ (or $Cp^*_2W(CD_3)_2$) in benzene-d_6 was heated at 220 °C in a sealed NMR tube (CARE!). The product was characterized as $\{Cp^*(\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2\}W$ by comparison of the ^1H NMR data with that in the literature.[7]

Reactions of $Cp^*_2WH_2$ with D_2 and $Cp^*_2WD_2$ with H_2. Solutions of either $Cp^*_2WH_2$ or $Cp^*_2WD_2$ (benzene-d_6) were sealed under D_2 or H_2 (4 atm), respectively, in 5-mm NMR tubes. The solutions were heated at 140 °C (CARE!), and exchange processes were monitored by ^1H NMR spectroscopy.

Thermal Decomposition of $Cp^*_2W(OH)H$. A solution of $Cp^*_2W(OH)H$ in benzene-d_6 was heated at 60 °C for ca. 1 day. The products were characterized by comparison of the ^1H NMR data with those of authentic samples.[6] The decomposition of the ^{17}O-labeled derivative $Cp^*_2W(^{17}OH)H$ was also monitored by ^{17}O NMR spectroscopy, which confirmed the formation of $H_2{}^{17}O$.

Acknowledgment. We thank Professor Jack Norton for providing information prior to publication. This work was supported by the National Science Foundation (Grant No. CHE-8600875) and by Shell Companies Foundation, which are gratefully acknowledged. G.P. acknowledges support through a NATO Postdoctoral Fellowship administered through the Science and Engineering Research Council (U.K.).

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