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Intramolecular Hydrogen Exchange among the Coordinated Methane Fragments of $Cp_2W(H)CH_3$. Evidence for the Formation of a σ Complex of Methane Prior to Elimination

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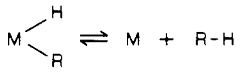
Abstract: NMR examination at 45–50 °C of a solution containing appropriate isotopically labeled derivatives of $Cp_2W(H)CH_3$ shows intramolecular hydrogen exchange between the hydride and methyl ligands of individual molecules, combined at high concentrations with intermolecular hydride exchange. Because of this intermolecular hydride exchange, methane elimination, although intramolecular, appears to be intermolecular at high concentrations. Comparison of the rate of CH_4 elimination from $Cp_2W(H)CH_3$ with the rate of CD_4 elimination from $Cp_2W(D)CD_3$ shows an inverse isotope effect of 0.7 at 72.6 °C. The reversible formation of a σ complex of methane as an intermediate in the elimination process is the most plausible explanation for the H/CH_3 scrambling and for the inverse isotope effect.

A growing body of thermodynamic evidence[1] shows that there is little energy difference between alkyl hydride complexes and the corresponding combinations of alkanes and lower valent metals. Equilibria of the type in eq 1 are often approximately thermo-



(1)

neutral. Thus alkane elimination from an initial alkyl hydride complex can be used to generate an intermediate that is capable of oxidatively adding other C–H bonds and thereby of forming new alkyl hydride complexes.[2-4]

Reductive elimination of an alkane from an alkyl hydride complex[5] had only been directly observed for complexes of the later transition metals (e.g., $PtL_2(H)CH_3$,[6] $IrL_2Cl(H)$(carboranyl),[7] and $[IrL_4(H)R]^+$[8]) when we decided to study the reductive elimination of methane from the tungsten alkyl hydride complex $Cp_2W(H)CH_3$.[9] Photolysis of $Cp_2W(H)CH_3$ under matrix isolation conditions had been found to generate tungstenocene (Cp_2W),[10] and Green and co-workers had reported that, upon thermolysis in solution, $Cp_2W(H)CH_3$ generated a species capable of reacting with aromatic C–H bonds.[9]

In a preliminary communication[11] we reported the preparation of $Cp_2W(D)CH_3$ and $Cp_2W(H)CD_3$ and the results of crossover experiments showing that thermal methane elimination from $Cp_2W(H)CH_3$ was indeed intramolecular. We also reported an unexpected complication, the exchange of hydrogen (which will be called global exchange in the present manuscript) among all of the methyl and hydride ligands in concentrated solutions of $Cp_2W(H)CH_3$. Since our initial report, similar exchange processes have been observed: (a) the hydride ligand of $Cp^*Ir(PMe_3)(H)(C_6H_{11})$ exchanges with the α hydrogen of its cyclohexyl ligand prior to the elimination of cyclohexane;[2b] (b) the hydride ligand of $Cp^*Rh(PMe_3)(H)R$ exchanges with the α hydrogens of its R = ethyl and R = cyclopropyl ligands prior to the elimination of R–H;[2d] (c) the hydride ligand of $[Cp_2Re(H)CH_3]^+$ exchanges with its methyl ligand hydrogens prior to the elimination of methane;[12] (d) the hydride ligand of $Cp^*{}_2W(H)CH_3$ exchanges with its methyl ligand hydrogens prior to the elimination of methane.[13] We now report the details of the preparation of various deuterium-substituted derivatives of $Cp_2W(H)CH_3$, a comprehensive study of the mechanism responsible for the reductive elimination of methane from it, and the elucidation of the processes responsible for global hydrogen exchange among all of the methyl and hydride ligands in a solution of it.

Results

Preparation of $Cp_2W(H)CD_3$. This compound was prepared straightforwardly by the route used by Cooper, Green, and Mahtab[9a] for the synthesis of $Cp_2W(H)CH_3$. CD_3MgBr[14] was used for the preparation of $Cp_2W(CD_3)_2$ (eq 2), which was then transformed into $Cp_2W(H)CD_3$ (eq 3 and 4).

$$Cp_2WCl_2 + CD_3MgBr \xrightarrow{25\ ^\circ C,\ Et_2O} Cp_2W(CD_3)_2 \qquad (2)$$

$$Cp_2W(CD_3)_2 + PhCO_2H \xrightarrow[\text{heptane}]{60\ ^\circ C,\ 1\ h} Cp_2W(CD_3)(O_2CPh) \qquad (3)$$

$$Cp_2W(CD_3)(O_2CPh) + Na[AlH_2(OCH_2CH_2OCH_3)_2] \rightarrow Cp_2W(H)CD_3 \qquad (4)$$

In our hands, $Cp_2W(H)CH_3$ and its labeled derivatives are at best 99% pure, with hydride resonances due to at least 1–2% Cp_2WH_2 and/or Cp_2WHD always detected by ^1H NMR.

Attempted Preparation of $Cp_2W(D)CH_3$ by Deuteride Reduction of $Cp_2W(CH_3)(O_2CPh)$.[15] We attempted the preparation of

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(1) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

(2) (a) Bergman, R. G. *Science* **1984**, *223*, 902. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537, and references therein. (c) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856. (d) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346, 7346–7355, and references therein.

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(5) A list of known alkyl hydride complexes has been given in ref 11.

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(8) (a) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (b) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221, and references therein.

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(12) Gould, G. L.; Heinekey, M., personal communication of unpublished work.

(13) Parkin, G.; Bercaw, J. E., personal communication of unpublished work.

(14) Although CD_3MgI is experimentally the simplest deuteriomethyl Grignard reagent to prepare (CD_3I, unlike CD_3Br, boils above room temperature), methyl magnesium iodide gives a negligible yield of dimethyl tungstenocene from Cp_2WCl_2. In contrast, CH_3MgCl and CH_3MgBr are both known[9a] to be effective in the alkylation of Cp_2WCl_2.

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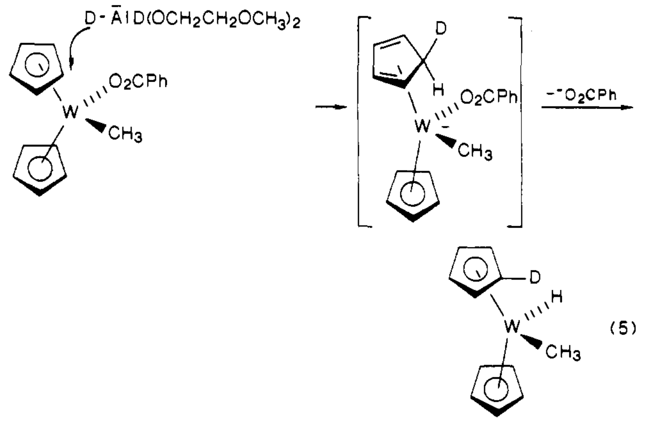
$Cp_2W(D)CH_3$ from $Cp_2W(CH_3)(O_2CPh)$ and $Li[AlD_2(OCH_2CH_2OCH_3)_2]$. The mass spectrum of the product contained a parent ion with an appropriate isotope pattern and a mass 1 unit greater than that of isotopically normal $Cp_2W(H)CH_3$; however, it also contained a fragment ion with a mass 1 unit greater than that of isotopically normal Cp_2W^+, suggesting that the deuterium had become incorporated into a cyclopentadienyl ring instead of attached to the tungsten. This implication was confirmed by the presence of a weak ν_{C-D} band at 2310 cm^{-1} in the IR spectrum of the product. $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4D)W(H)CH_3$ is presumably formed by exo deuteride transfer onto the cyclopentadienyl ring, followed by endo hydride transfer onto the tungsten as the benzoate anion leaves (eq 5).



(5)

In retrospect, the exo transfer of deuteride from $[AlD_2(OR)_2]^-$ onto a cyclopentadienyl ligand is easily understood. The tungsten in $Cp_2W(CH_3)(O_2CPh)$ is coordinatively saturated, and an incoming nucleophile must therefore attack a cyclopentadienyl ligand directly, giving exo stereochemistry. Such exo attack has been noted for the transfer of hydride onto the benzene ligand in $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]^+$ and the cyclohexadienyl ligand in $(\eta^5\text{-}C_6H_7)Mn(CO)_3$,[16] onto the cyclohexadienyl ligand in $[(\eta^5\text{-}C_6H_6\text{-}1\text{-}CO_2Me)Fe(CO)_3]^+$,[17] and onto the cyclopentadienyl ligand in $[CpFe(Ph_2PCH_2CH_2PPh_2)CO]^+$.[18,19] A result similar to that in eq 5, where D, originally transferred exo onto an η^5-cyclopentadienyl ring, remains on an $\eta^5\text{-}C_5H_4D$ ring after migration of the endo H, has been reported for the reaction of $[DBEt_3]^-$ with $[CpFe(CO)PPh_3(MeC{\equiv}CCO_2Et)]^+$; the migrating H is transferred onto the coordinated acetylene to form a vinyl ligand.[20]

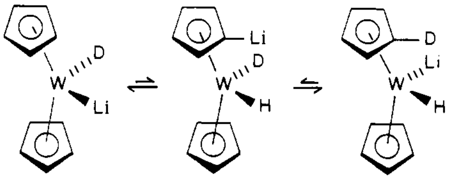
Attempted Preparation of $Cp_2W(D)CH_3$ from Cp_2WD_2. We then attempted to prepare $Cp_2W(D)CH_3$ by lithiation and methylation of the known[21] Cp_2WD_2. In our hands the lithiation of Cp_2WH_2 by *n*-BuLi was unsuccessful in freshly distilled and completely oxygen-free toluene; we obtained the known[22] $[Cp_2WHLi]_4$ only after the addition of 2 or 3 drops of dimethoxyethane (glyme) (eq 6). Quenching the $[Cp_2WHLi]_4$ with D_2O

$$Cp_2WH_2 + BuLi \xrightarrow[+\text{ trace glyme}]{\text{toluene}} [Cp_2WHLi]_4 + BuH \qquad (6)$$

put deuterium only on the tungsten and not on the cyclopentadienyl rings, as shown by the absence of ν_{C-D} from the IR spectrum of the resulting material. As quenching had placed deuterium only at the position that had been occupied by lithium, we concluded that such quenching experiments accurately reflected the site of lithiation.

Thus, when D_2O quenching of lithiated Cp_2WD_2 gave material with ^1H on tungsten, we knew that H/D scrambling must have occurred prior to quenching and therefore that lithiation of Cp_2WD_2 must have resulted in deuterium scrambling between the cyclopentadienyl ring and the tungsten. We confirmed this conclusion by finding ν_{W-H} at 1750 cm^{-1} in the IR spectrum of lithiated Cp_2WD_2.

These results are easily explained if an isomer of $[Cp_2WHLi]_4$, with the cyclopentadienyl rings lithiated, is kinetically accessible from $[Cp_2WHLi]_4$ even though it is thermodynamically less stable than the latter (eq 7). The suggestion of such a ring-lithiated intermediate is plausible in view of a report that the cyclopentadienyl rings of tungstenocene complexes can be lithiated under some conditions.[23] A kinetic preference for lithiation of a cyclopentadienyl ring despite a thermodynamic preference for lithiation of an M–H bond has been directly observed for $CpRe(PPh_3)(NO)H$.[24]



(7)

Treatment of $[Cp_2WHLi]_4$ with MeI gave a mixture of $Cp_2W(Me)I$[25] and Cp_2WI_2.[26] Treatment of $[Cp_2WHLi]_4$ with $MeOSO_2F$ resulted in vigorous evolution of methane, as did the treatment of Cp_2WH_2 with $MeOSO_2F$. Treatment of a benzene suspension of $[Cp_2WHLi]_4$ with methyl tosylate gave a small amount of impure $Cp_2W(H)CH_3$. As proton-transfer side reactions complicate any attempt to prepare a methyl hydride complex by methylation of a hydride anion[27] and as it seemed likely that these side reactions were exacerbated by the heterogeneous nature of the $[Cp_2WHLi]_4$/MeOTs reaction, we sought a way to prepare a homogeneous solution that contained $[Cp_2WHLi]_4$ or its equivalent.

The use of 1,1,4,7,7-pentamethyldiethylenetriamine (PMDT) to make $[Cp_2WHLi]_4$ soluble in nonpolar organic solvents was suggested by its successful use[28] with $[Cp_2MoHLi]_4$. $[Cp_2WHLi]_4$ did dissolve in toluene in the presence of 1 equiv of PMDT, and the addition of this solution to an excess of methyl tosylate did produce $Cp_2W(H)CH_3$ in reasonable yield (eq 8), but the removal

$$[Cp_2WHLi]_4 \xrightarrow[\text{toluene}]{\text{PMDT}} \xrightarrow{\text{excess MeOTs}} Cp_2W(H)CH_3 \qquad (8)$$

of the MeOTs and PMDT (particularly the latter) from the

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(15) $Li[AlH_2(OCH_2CH_2OCH_3)_2]$ (obtained from $LiAlH_4$ and $CH_3OCH_2CH_2OH$) and $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ gave similar results in the preparation of $Cp_2W(H)CH_3$ from $Cp_2W(CH_3)(O_2CPh)$, demonstrating that the nature of the cation was unimportant. We obtained $Li[AlD_2(OCH_2CH_2OCH_3)_2]$ by treating the commercially available $LiAlD_4$ with 2 equiv of 2-methoxyethanol.

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(18) Davies, S. G.; Hibberd, J.; Simpson, S. J.; Thomas, S. E.; Watts, O. *J. Chem. Soc., Dalton Trans.* **1984**, 701–9.

(19) Endo attack by a nucleophile on a coordinated polyene is possible only when there is initial nucleophilic attack on another ligand (i.e., a carbonyl) or on the metal itself. Thus, a formyl intermediate, which at higher temperatures transfers its formyl hydrogen to the endo position of an $\eta^4\text{-}C_5H_6$ ligand, can be seen at −78 °C when $[CpFe(Ph_2PCH_2CH_2PPh_2)CO]^+$ is attacked by $LiAlH_4$,[18] and a formyl intermediate is probably involved in the endo addition of hydride to $[(\eta^5\text{-}C_6H_6R)Mn(CO)_2(NO)]^+$: Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. *J. Am. Chem. Soc.* **1985**, *107*, 2388–93.

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(23) Cooper, R. L.; Green, M. L. H.; Moelwyn-Hughes, J. T. *J. Organomet. Chem.* **1965**, *3*, 261. Note that deuterium scrambling between the cyclopentadienyl ring and the methyl does not occur when Cp_2MoD_2 is lithiated.[22a]

(24) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 283; *J. Am. Chem. Soc.* **1988**, *110*, 6110.

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(27) Successful methylation of MH^- must be faster than $M(H)CH_3/MH^-$ proton transfer. For a discussion, see: Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.

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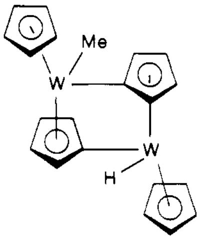
product proved to be difficult and could be accomplished only at the cost of a decrease in the isolated yield; the byproduct Li(PMDT)OTs was quite soluble in organic solvents and was not completely removed by extraction with water.

Preparation of $Cp_2W(D)CH_3$ by Lithiation of $Cp_2W(H)CH_3$. The fact that Cp_2WH_2 could be lithiated (eq 6) suggested that lithiation of $Cp_2W(H)CH_3$ might be possible. Indeed, treatment of a benzene solution of $Cp_2W(H)CH_3$ with *n*-BuLi in the presence of 1 or 2 drops of glyme gave a precipitate of yellow crystals. By analogy to the Cp_2WH_2/BuLi case, we expected that (1) the tungsten would again be the thermodynamically preferred site of lithiation and that (2) D_2O quenching would again place deuterium only at the position that had been occupied by lithium. Upon addition of a suspension of these crystals to a benzene/D_2O mixture (eq 9), we finally obtained $Cp_2W(D)CH_3$, with ν_{W-D} at 1345 cm^{-1}.

$$Cp_2W(H)CH_3 + BuLi \xrightarrow[\text{+ trace glyme}]{\text{toluene}} \xrightarrow{D_2O} Cp_2W(D)CH_3 \quad (9)$$

Similarly, lithiation followed by a D_2O quench converted $Cp_2W(H)CD_3$ to $Cp_2W(D)CD_3$.

Elimination of Methane from $Cp_2W(H)CH_3$. Use of Acetonitrile as Trap. As Cooper, Green, and co-workers had already reported,[9] methane was eliminated when a solution of $Cp_2W(H)CH_3$ was heated. In cyclohexane these workers had observed[9a,b] the formation of dinuclear products **1** and **2**; it seemed a reasonable hypothesis that Cp_2W was being formed and was reacting with the C–H bonds of the cyclopentadienyl rings of $Cp_2W(H)CH_3$ in the absence of a sufficiently reactive substrate. As expected on the basis of this observation, we found a complex mixture of tungsten-containing products to be formed when we heated concentrated solutions of $Cp_2W(H)CH_3$ in unreactive solvents.



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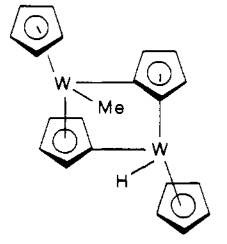

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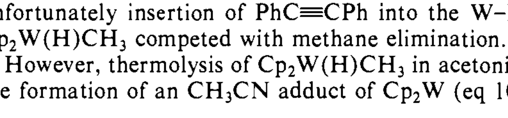
Green and co-workers had also reported[9a] that $Cp_2W(H)Ph$ was formed when a 3×10^{-3} M solution $Cp_2W(H)CH_3$ in benzene was heated, so we thought that solvent benzene might be capable of intercepting the Cp_2W fragment effectively. However, the NMR kinetics we planned required the use of C_6D_6 instead of C_6H_6, and C_6D_6 at least proved ineffective as a trap at high concentrations of $Cp_2W(H)CH_3$: thermolysis of a 0.2 M solution of $Cp_2W(H)CH_3$ in C_6D_6 at 74 °C gave a complex mixture of products. We therefore sought a species that would serve as an effective trap when added to a benzene solution of $Cp_2W(H)CH_3$. Abis, Sen, and Halpern had used diphenylacetylene for this purpose in their study of methane elimination from $PtL_2(H)CH_3$,[6] and we therefore tried diphenylacetylene with $Cp_2W(H)CH_3$; unfortunately insertion of PhC≡CPh into the W–H bond of $Cp_2W(H)CH_3$ competed with methane elimination.

However, thermolysis of $Cp_2W(H)CH_3$ in acetonitrile led to the formation of an CH_3CN adduct of Cp_2W (eq 10). An η^2



(10)

structure for the coordinated CH_3CN was indicated by the ν_{C-N} at 1725 cm^{-1} in its IR spectrum,[29a] a value far below that (2280 cm^{-1}) of free CH_3CN. An X-ray crystal structure[29b] has confirmed that the CH_3CN ligand is η^2 in the analogous molybdenum compound, $Cp_2Mo(CH_3CN)$.

Table I. Percentages of Various Deuterated Methanes Formed upon Thermolysis of $Cp_2W(D)CH_3$[a] and $Cp_2W(H)CD_3$[a] at 82.5 °C

CH_4	0 ± 2	CHD_3	48 ± 2
CH_3D	43 ± 3	CD_4	4 ± 2
CH_2D_2	6 ± 3		

[a] Each component 0.67 mM in toluene 90% toluene/10% CH_3CN.

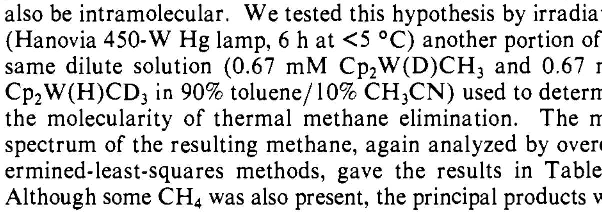
Table II. Percentages of Various Deuterated Methanes Formed upon Photolysis of $Cp_2W(D)CH_3$[a] and $Cp_2W(H)CD_3$[a]

CH_4	14 ± 2	CHD_3	42 ± 2
CH_3D	29 ± 3	CD_4	8 ± 2
CH_2D_2	7 ± 3		

[a] Each component 0.67 mM in 90% toluene/10% CH_3CN.

We therefore tried 10% acetonitrile as a trap in aromatic solvents and found the acetonitrile to be an effective trap even at high concentrations of $Cp_2W(H)CH_3$. The rate of disappearance of $Cp_2W(H)CH_3$ in C_6D_6 was unaffected by the addition of CD_3CN: in preliminary experiments at 70 °C, the observed first-order rate constant was 4.5×10^{-5} s^{-1} with 10% CD_3CN added and 4.2×10^{-5} s^{-1} without it. All subsequent studies were therefore carried out in aromatic solvents with 10% acetonitrile.

Intramolecular Thermal and Photochemical Methane Elimination from $Cp_2W(H)CH_3$ at Low Concentrations. While designing the trapping experiments above, we had assumed that tungstenocene was formed by intramolecular elimination of methane from $Cp_2W(H)CH_3$. However, recalling our earlier finding that methane elimination from *cis*-$Os(CO)_4(H)CH_3$ was intermolecular,[30] we began our study of methane elimination from $Cp_2W(H)CH_3$ by checking to see if the latter elimination was indeed intramolecular. An equimolar solution in 90% toluene/10% CH_3CN of $Cp_2W(D)CH_3$ and $Cp_2W(H)CD_3$, each 0.67 mM, was heated for 6 h at 82.5 °C. The mass spectrum of the resulting methane was fitted to the known[31] mass spectra of CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 by overdetermined-least-squares methods, with the results shown in Table I. The predominance of CH_3D and CHD_3 confirmed that methane elimination had been intramolecular (eq 11). The organometallic product was, as expected, $Cp_2W(\eta^2\text{-}CH_3CN)$.



(11)

In view of the photochemical formation of Cp_2W from $Cp_2W(H)CH_3$ under matrix isolation conditions,[10] we expected that *photochemical* methane elimination from $Cp_2W(H)CH_3$ would also be intramolecular. We tested this hypothesis by irradiating (Hanovia 450-W Hg lamp, 6 h at <5 °C) another portion of the same dilute solution (0.67 mM $Cp_2W(D)CH_3$ and 0.67 mM $Cp_2W(H)CD_3$ in 90% toluene/10% CH_3CN) used to determine the molecularity of thermal methane elimination. The mass spectrum of the resulting methane, again analyzed by overdetermined-least-squares methods, gave the results in Table II. Although some CH_4 was also present, the principal products were CH_3D and CHD_3; the photochemical methane elimination had thus been predominantly intramolecular (eq 12). No identifiable organometallic products were recovered.

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(29) (a) η^2 structures have recently been established by X-ray studies for nitrile complexes with C–N stretching frequencies of 1758 and 1781 cm^{-1}: Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650–660. (b) Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2017–2019.

(30) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376.

(31) American Petroleum Institute Mass Spectroscopic Tables, Series Numbers 455–458. Another set of mass spectra for methane-d_n have just been published, along with a detailed discussion of the mass spectroscopic determination of alkane isotopic compositions: Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3156.

$$\begin{bmatrix} Cp_2W(D)CH_3 \\ + \\ Cp_2W(H)CD_3 \end{bmatrix} \xrightarrow[CH_3CN/toluene]{h\nu} CH_3D + CHD_3 \qquad (12)$$

The intramolecularity of thermal methane elimination in dilute solution was further checked by eliminating methane at 82.9 °C from a benzene/acetonitrile solution of $Cp_2W(D)CD_3$ and $Cp_2W(H)^{13}CH_3$. The former was prepared from $Cp_2W(H)CD_3$, by the method used above to prepare $Cp_2W(D)CH_3$ from $Cp_2W(H)CH_3$, and contained 88% D on W; the latter was prepared from $^{13}CH_3Br$ by the method used above for the preparation of $Cp_2W(H)CD_3$. The principal isotopically labeled methanes observed were $^{13}CH_4$ (40 ± 6%), CD_4 (42 ± 6%), and CHD_3 (14 ± 6%), as expected for intramolecular elimination (eq 13). (The CHD_3 was expected from the 12% $Cp_2W(H)CD_3$ present in the initial $Cp_2W(D)CD_3$.)

$$\begin{bmatrix} Cp_2W(D)CD_3 \\ + \\ Cp_2W(H)^{13}CH_3 \end{bmatrix} \xrightarrow{\Delta} CD_4 + {}^{13}CH_4 \qquad (13)$$

Global Scrambling Prior to Methane Elimination from $Cp_2W(H)CH_3$ at Higher Concentrations. In solutions more concentrated than 0.01 M, NMR observations showed that isotopically labeled derivatives of $Cp_2W(H)CH_3$ underwent an unexpected label-scrambling process prior to methane elimination. After several hours at 40 °C the ^1H NMR of a 0.61 M solution of $Cp_2W(H)CD_3$ showed a decrease in its hydride resonance and the appearance of a new signal at δ 0.02 due to methyl ligand hydrogens. Similarly, after several hours at 45 °C the ^2H NMR signal of a 0.058 M solution of $Cp_2W(D)CH_3$ decreased, and a signal due to methyl ligand ^2H appeared. While it was tempting to attribute these results solely to the operation of the intramolecular equilibria in eq 14 and 15, further experiments showed that other equilibria also operated *at these higher concentrations*.

$$Cp_2W(H)CD_3 \overset{K_1}{\rightleftharpoons} Cp_2W(D)CHD_2 \qquad (14)$$

$$Cp_2W(D)CH_3 \overset{K_2}{\rightleftharpoons} Cp_2W(H)CH_2D \qquad (15)$$

In order to check the molecularity of the hydride/methyl ligand scrambling process, we performed a double-labeling experiment. The methyl ligands on some molecules were labeled with ^{13}C and the methyl ligands on others were labeled with ^2H, so that we would know if labels traveled from molecule to molecule. We heated an NMR tube containing a C_6D_6 solution of $Cp_2W(H)^{13}CH_3$ (66 mM) and $Cp_2W(H)CD_3$ (132 mM) at 47.3 °C and monitored the reaction by ^1H and ^{13}C NMR. The appearance of ^2H splitting in the methyl ligand signal in the ^{13}C NMR spectrum, and the disappearance of ^{13}C splitting in the methyl ligand signal in the ^1H NMR spectrum, showed that H/D scrambling was occurring *among molecules* as well as between the methyl and hydride ligands of each molecule (eq 16). The overall process scrambled H and D among all methyl and hydride ligands in a concentrated solution of $Cp_2W(H)CH_3$ and will be called "global" H/D scrambling.

$$\begin{aligned} &Cp_2W(H)^{13}CH_3 + Cp_2W(H)CD_3 \rightarrow \\ &\underset{A}{W(H)^{13}CH_3} + \underset{B}{W(H)^{13}CH_2D} + \underset{C}{W(H)^{13}CHD_2} + \underset{D}{W(H)^{13}CD_3} \\ &\underset{E}{W(D)^{13}CH_3} + \underset{F}{W(D)^{13}CH_2D} + \underset{G}{W(D)^{13}CHD_2} + \underset{H}{W(D)^{13}CD_3} \\ &\underset{I}{W(H)^{12}CH_3} + \underset{J}{W(H)^{12}CH_2D} + \underset{K}{W(H)^{12}CHD_2} + \underset{L}{W(H)^{12}CD_3} \\ &\underset{M}{W(D)^{12}CH_3} + \underset{N}{W(D)^{12}CH_2D} + \underset{O}{W(D)^{12}CHD_2} + \underset{P}{W(D)^{12}CD_3} \end{aligned} \qquad (16)$$

Unfortunately the distance of this $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ system from equilibrium, and its slow decomposition at 47.3 °C, made it impractical to continue monitoring the experiment until an experimentally observable equilibrium had been established.

Calculation of K_1 and K_2 from NMR Observation of Concentrated Solutions of $Cp_2W(H)CD_3$ or $Cp_2W(D)CH_3$. Intermolecular H/D scrambling at higher concentrations complicated the determination of K_1 and K_2. Such concentrations were required for the accurate measurement of relative signal intensities, but the resulting intermolecular scrambling meant that a solution that initially contained only $Cp_2W(H)CD_3$ would eventually contain not only $Cp_2W(D)CHD_2$ but all of the species on the right of eq 17. Whereas the ratio of the integrated intensity of the methyl ^1H NMR signal to that of the hydride ^1H NMR signal would be equal to K_1 if only $Cp_2W(H)CD_3$ and $Cp_2W(D)CHD_2$ were present, that ratio will differ from the true K_1 if intermolecular scrambling has led to the formation of the other species in eq 17.

$$\begin{aligned} Cp_2W(H)CD_3 \rightleftharpoons{} & W(D)CHD_2 + W(D)CD_3 + W(H)CHD_2 \\ & + W(D)CH_2D + W(H)CH_2D + W(D)CH_3 + W(H)CH_3 \end{aligned} \qquad (17)$$

Similarly, a concentrated solution of $Cp_2W(D)CH_3$ will eventually contain not only $Cp_2W(H)CH_2D$ but all of the species in eq 17. Whereas the ratio of the integrated intensity of the methyl ^2H NMR signal to that of the W–D ^2H NMR signal would be equal to K_2 if only $Cp_2W(D)CH_3$ and $Cp_2W(H)CH_2D$ were present, that ratio will differ from the true K_2 if intermolecular scrambling has led to the formation of the other species in eq 17.

The true values of K_1 and K_2 can be calculated from the observed integrated intensity ratios by taking intermolecular scrambling into account; details are given in Appendix I. The correction is small—no larger than the difference between two independent measurements of the intensity ratios—and gives K_1 as 1.4 (2).

Evaluation of the Rate Constants for Global Scrambling in the $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ System. We were now able to obtain more information from the results of the double-labeling $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ experiment, shown in eq 16, which had demonstrated global H/D scrambling. Our inability to continue monitoring this experiment until equilibrium was established had made it impossible to determine the rates at which the various parts of the system approached equilibrium. Now, however, knowing K_1,[32] we were able to calculate the H/D label distribution for this concentrated (total tungsten 0.2 M) $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ system at infinite time and thus the rate constants for its approach to equilibrium at 47.3 °C.

From each ^{13}C NMR spectrum taken during the reaction we computed C_1 (eq 18), the fraction of all methyl ^{13}C NMR signals that belonged to undeuterated methyl groups ($^{13}CH_3$); the decrease of C_1 below its initial value of unity reflected the transfer of D onto ^{13}C by intermolecular processes. From each ^1H NMR spectrum taken during the reaction we computed H_1 (eq 19), the fraction of all methyl and hydride ^1H NMR signals that belonged to ^{12}C methyl groups ($^{12}CH_nD_{3-n}$); the increase of H_1 above its initial value of zero reflected the transfer of H onto ^{12}C by intramolecular processes (i.e., from the H of $Cp_2W(H)^{12}CD_3$) as well as by intermolecular processes.

$$C_1 = \frac{A}{A + B + C + D + E + F + G + H} \qquad (18)$$

$$H_t = \frac{3I+2J+K+3M+2N+O}{4A+3B+2C+D+3E+2F+G+4I+3J+2K+L+3M+2N+O} \qquad (19)$$

The expected values of C_∞ and H_∞ were obtained by calculating the distribution of deuterium between the methyl and hydride sites

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[32] Although K_1 had been most accurately determined at 45.0 °C, K_1 showed no temperature dependence greater than experimental error between 40 and 50 °C; we therefore took K_1 as 1.4 (2) at 47.3 °C, the temperature of the double-labeling $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ experiment.

at infinite time (see Appendix II for details). The rate constants k_C and k_H, defined by eq 20 and 21, were then calculated from eq 22 and 23 (the integrated forms of eq 20 and 21).

$$\frac{-\mathrm{d}(C_t - C_\infty)}{\mathrm{d}t} = k_C(C_t - C_\infty) \qquad (20)$$

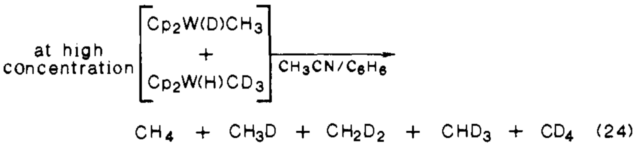
$$\frac{-\mathrm{d}(H_t - H_\infty)}{\mathrm{d}t} = k_H(H_t - H_\infty) \qquad (21)$$

$$\ln (C_t - C_\infty) = -k_C t + \text{constant} \qquad (22)$$

$$\ln |H_t - H_\infty| = -k_H t + \text{constant} \qquad (23)$$

At 47.3 °C, k_C was 2.8×10^{-5} s^{-1} and k_H was 2.9×10^{-5} s^{-1}; the two rate constants were essentially equal. As k_C detected only intermolecular scrambling, whereas k_H detected intramolecular scrambling as well, it was clear that, in this concentrated $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ solution, intermolecular H/D scrambling processes operated much faster than intramolecular ones.

Apparent Intermolecular Methane Elimination from $Cp_2W(H)CH_3$ at Higher Concentrations. At higher concentrations, where global H/D scrambling occurred before methane elimination, the latter inevitably *appeared* to be intermolecular. Thus a 10% CH_3CN/90% C_6H_6 solution of $Cp_2W(D)CH_3$ (14.0 mM) and $Cp_2W(H)CD_3$ (9.4 mM) gave appreciable CH_4, CD_2H_2, and CD_4 after 3 h at 82 °C (eq 24). When the mass spectrum of the evolved methanes was analyzed by the usual overdetermined-least-squares methods, these intermolecular products were collectively 48% of the total.



$$\text{at high concentration} \begin{bmatrix} Cp_2W(D)CH_3 \\ + \\ Cp_2W(H)CD_3 \end{bmatrix} \xrightarrow[CH_3CN/C_6H_6]{} CH_4 + CH_3D + CH_2D_2 + CHD_3 + CD_4 \qquad (24)$$

Independent Observation of Intermolecular Hydride Exchange at Higher Concentrations. The fact that global H/D scrambling was facile at high concentrations but not at low ones suggested a bimolecular mechanism with second-order kinetics. We therefore checked for intermolecular H/D exchange between W–H and W–D bonds.

Facile exchange between $Cp_2W(H)CH_3$ and Cp_2WD_2 was observed by ^1H NMR (eq 25). When a C_6D_6 solution of

$$Cp_2W(H)CH_3 + Cp_2WD_2 \rightleftharpoons Cp_2W(D)CH_3 + Cp_2WHD \qquad (25)$$

$Cp_2W(H)CH_3$ (20 mM) and Cp_2WD_2 (14 mM) was heated at 45 °C for 2 h, the hydride resonance of the dihydride complex (i.e., of Cp_2WH_2 and Cp_2WHD) increased, with a concomitant decrease in the hydride resonance of the methyl hydride complex. Similarly, when a C_6H_6 solution of $Cp_2W(D)CD_3$ (133 mM) and Cp_2WH_2 (115 mM) was heated at 47 °C for 5 h, the ^2H NMR resonance due to W-bound D in the deuterated methyl hydride complex decreased, while a signal due to D ligands in the dihydride complex (i.e., in Cp_2WHD or in Cp_2WD_2) appeared. These preliminary results convinced us to investigate the kinetics of the exchange of hydride ligands between $Cp_2W(H)CH_3$ and Cp_2WD_2.

Samples were prepared that contained various concentrations of Cp_2WD_2 and $Cp_2W(H)CH_3$ in 10% CH_3CN/90% toluene-d_8, along with an internal standard (dodecane). The first-order rate constants, $k_{\mathrm{equil}\,25}$, for the approach of these samples to isotopic equilibrium at 48.2 °C were obtained by monitoring them by ^1H NMR. Equivalent rate constants were obtained from the increase in the dihydride W–H signal and the decrease in the methyl hydride W–H signal. The results are given in Table III.

The general form of the McKay equation[33] for isotope exchange reactions predicts that the first-order rate constant $k_{\mathrm{equil}\,25}$ will be given by eq 26 if the chemical reaction that produces exchange is associative, with a rate law that is second-order overall and first-order in each reactant. The second-order rate constant for that reaction, the exchange of hydride ligands between $Cp_2W(H)CH_3$ and Cp_2WH_2, is k_{HH}. (We must neglect any isotope effects on k_{HH}.) The factor of 2 arises when there are two equivalent exchangeable sites on one reactant, as there are on Cp_2WD_2. The observed values of $k_{\mathrm{equil}\,25}$ and of the initial concentrations of Cp_2WD_2 and $Cp_2W(H)CH_3$ in Table III fit eq 26, with k_{HH} equal to 6.7 (4) $\times 10^{-3}$ M^{-1} s^{-1} at 48.2 °C.

$$k_{\mathrm{equil}\,25} = (2[Cp_2WD_2]_{t=0} + [Cp_2W(H)CH_3]_{t=0})k_{HH} \qquad (26)$$

Table III. Rate Constants for Approach to Isotopic Equilibrium between Cp_2WD_2 and $CP_2W(H)CH_3$[a]

$[Cp_2WD_2]_{t=0}$, M	$[Cp_2W(H)CH_3]_{t=0}$, M	$10^4k_{\mathrm{equil}\,25}$, s^{-1}	10^3k_{HH},[b] M^{-1} s^{-1}
0.053	0.042	9.20	6.22
0.123	0.147	27.9	7.10
0.033	0.055	8.17	6.75
			av 6.7 (4)

[a] Measured at 48.2 °C in 90:10 toluene-d_8/CH_3CN. [b] Calculated from eq 26.

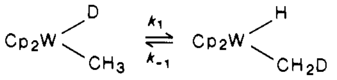
Table IV. Rate Constants for Elimination of Methane from $Cp_2W(H)CH_3$[a]

T, °C	$10^4k_{CH_3-H}$	$10^2[Cp_2W(H)CH_3]_{t=0}$
70.3	0.97 ± 0.2	2.6
76.2	1.8 ± 0.2	2.6
80.5	3.8 ± 0.1	1.6
80.5	4.1 ± 0.2	3.3
80.5	4.1 ± 0.2	6.5
85.3	4.6 ± 0.1	2.1
90.7	7.9 ± 0.1	2.1
96.3	14.1 ± 0.1	2.6

[a] In 10% CH_3CN/90% C_6D_6.

H/D exchange was also observed between Cp_2WD_2 and the hydride ligands of $Cp_2W(H)Ph$, $CpW(CO)_3H$, and $Os(CO)_4H_2$, with second-order rate constants k_{HH} of approximately 1.5×10^{-4} M^{-1} s^{-1} ($Cp_2W(H)Ph$), 0.1 M^{-1} s^{-1} ($CpW(CO)_3H$), and 7.9×10^{-4} M^{-1} s^{-1} ($Os(CO)_4H_2$) at 50 °C. ^1H and ^2H NMR showed that D from Cp_2WD_2 was never exchanged into the C–H bonds of any cyclopentadienyl ligands during exchange experiments. It was not possible to quantify the rate of hydride exchange among molecules of $Cp_2W(H)CH_3$ because of the lack of a change in hydride chemical shift during such self-exchange.

Observation of Intramolecular Hydrogen Scrambling in $Cp_2W(D)CH_3$ at Low Concentrations. Our discovery that associative exchange of hydride ligands among Cp_2W complexes was facile at high concentrations suggested that global hydrogen scrambling in solutions of $Cp_2W(H)CH_3$ might occur by a combination of intramolecular H/CH_3 scrambling and intermolecular H exchange. We therefore looked for H/CH_3 exchange at concentrations of $Cp_2W(H)CH_3$ where methane elimination was known to be *intramolecular* and where any *intermolecular* exchange prior to elimination was therefore impossible. Indeed, when a 0.7 mM solution of $Cp_2W(D)CH_3$ in 10% CH_3CN/90% toluene-d_8 was heated to 48 °C, ^1H NMR showed a decrease in the methyl resonance accompanied by an increase in the hydride resonance—evidence that the *intramolecular* equilibrium in eq 27 was establishing itself.



(27)

The extent of reaction was calculated from eq 28, where $I(\mathrm{methyl})_t$ was the integrated intensity of the methyl ^1H NMR resonance at time t and $I(\mathrm{hydride})_t$ was the integrated intensity of the hydride ^1H NMR resonance at time t. The rate constant $k_{\mathrm{equil}\,27}$ for approach to equilibrium, calculated from the extent of reaction as a function of time, was 2.5×10^{-5} s^{-1} at 48 °C. As the k_1/k_{-1} ratio from eq 27 was K_2 from eq 15 and as K_2 was equal to $9/K_1$ (as will be shown at the beginning of the Discussion section), k_1 (2×10^{-5} s^{-1}) and k_{-1} (5×10^{-6} s^{-1}) could be obtained by substituting $K_1 = 1.4$ into eq 29 and 30. The temperature range

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(33) McKay, H. A. C. *Nature* **1938**, *142*, 997; *J. Am. Chem. Soc.* **1943**, *65*, 702. (b) Harris, G. M. *Trans. Faraday Soc.* **1951**, *47*, 716. (c) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 50–55.

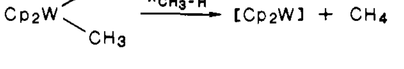
in which reaction 27 could be cleanly carried out was limited, and it was therefore impossible to obtain activation parameters for k_1 or k_{-1}.

$$\frac{[Cp_2W(H)CH_2D]_1}{[Cp_2W(D)CH_3]_1 + [Cp_2W(H)CH_2D]_1} = \frac{I(\text{hydride})_1}{[I(\text{methyl})_1 - 2I(\text{hydride})_1]/3 + I(\text{hydride})_1} = \frac{3}{1 + I(\text{methyl})_t/I(\text{hydride})_1} \quad (28)$$

$$K_2 = \frac{9}{K_1} = \frac{k_1}{k_{-1}} \quad (29)$$

$$k_{\text{equil }27} = k_1 + k_{-1} \quad (30)$$

Kinetics of Methane Elimination from $Cp_2W(H)CH_3$. Inverse Isotope Effect. With starting materials like $Cp_2W(H)CH_3$ or $Cp_2W(D)CD_3$, prior intra or intermolecular hydrogen exchange obviously had no effect on the rate of methane reductive elimination. The rate of the reductive elimination of the methanes in reactions 31 and 32 was determined by monitoring the disappearance of their ^{1}H NMR Cp resonances. These data showed satisfactory first-order kinetics, independent of the initial concentration of the methyl hydride complex (see for example the 80.5 °C $Cp_2W(H)CH_3$ data in Table IV). We thus measured $k_{CH_3\text{-}H}$ from 70 to 96 °C (Table IV) by the thermolysis of $Cp_2W(H)CH_3$ in 10% CD_3CN/90% C_6D_6. We obtained E_a = 25.8 (3) kcal/mol, log A = 12 (1), $\Delta H^\ddagger$ = 25.1 (3) kcal/mol, and $\Delta S^\ddagger$ = -4 (1) eu.



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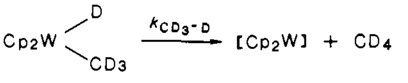


(32)

We also measured $k_{CH_3\text{-}H}$ and $k_{CD_3\text{-}D}$ carefully at 72.6 °C in CD_3CN and compared them to each other. The isotope effect was *inverse*, with $k_{CH_3\text{-}H}/k_{CD_3\text{-}D}$ equal to 0.75 (4).

Discussion

Equilibrium Isotope Effect. The value of the equilibrium constant K_1 in eq 14, 1.4 (2), is about that expected for an equilibrium with W–H and C–D bonds on the left replaced by W–D and C–H bonds on the right. Although statistically we would expect an equilibrium constant of 3, the equilibrium is shifted in the direction (to the left) that allows D to experience the larger force constants; the C–D stretching frequency is higher than the W–D one, and the C–D stretching force constant is higher than the W–D one.

For an equilibrium of the general type in eq 33, the expected equilibrium isotope effect can be calculated from eq 34,[34] if we

$$AH + BD \rightleftharpoons AD + BH \quad (33)$$

$$K(\text{calc}) = \sigma \prod_i \frac{e^{+1/2(u_i(AH)-u_i(AD))}}{e^{-1/2(u_i(BH)-u_i(BD))}} \quad (34)$$

$$K_1(\text{calc}) = 3e^{h/2k1(\nu_{WH}-\nu_{WD}-\nu_{CH}+\nu_{CD})} \quad (35)$$

neglect contributions other than those from differences in zero-point energy; σ is the statistical factor, u_i is $h\nu_i/kT$, and the product is over all vibrational modes i. If we (1) take A as tungsten and B as carbon, so that we are calculating K_1 and (2) consider only stretching frequencies (both because we do not know the bending force constants and because the latter are probably small), eq 34 simplifies to eq 35. Substitution of the experimental stretching frequencies gives K_1(calc) = 1.84 at 45.0 °C. This calculated value agrees reasonably well with the experimental methyl/hydride ^{1}H NMR ratio (1.6) from the $Cp_2W(H)CD_3/Cp_2W(D)CHD_2$ experiment and with the value of K_1 obtained after correcting for intermolecular exchange (1.4).

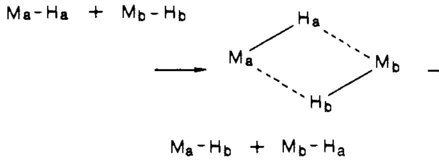
The equilibrium constant in eq 15, K_2, can be calculated from eq 34 if we designate A as carbon and B as tungsten. The resulting expression, eq 36, differs from eq 35 only in the sign of the exponential, i.e., in whether the isotope effect opposes or reinforces the statistical factor. The product of K_1 and K_2 is thus 9 (eq 37), and K_2(calc) is 4.88 at 45.0 °C. This calculated value is quite close to the experimental value (4.9) of the methyl/hydride ^{2}H NMR ratio in the $Cp_2W(D)CH_3/Cp_2W(H)CH_2D$ experiment.

$$K_2(\text{calc}) = 3e^{-h/2k1(\nu_{WH}-\nu_{WD}-\nu_{CH}+\nu_{CD})} \quad (36)$$

$$K_1(\text{calc})K_2(\text{calc}) = 9 \quad (37)$$

Equilibrium isotope effects of similar origin and magnitude are common in organometallic systems that interconvert M–H and M–C bonds. Recent examples, statistically adjusted so that they can be compared with K_1, are 1.1 for (Rh-D,C-H)/(Rh-H,C-D),[35a] 1.9 for (Pt-D,C-H)/(Pt-H,C-D),[35b] 1.4 for (Ru-D,C-H)/(Ru-H,C-D),[35c] and 2.1 for $(\mu\text{-H})_2(\mu\text{-D})Fe_3CH/(\mu\text{-H})_3Fe_3CD$.[35d] (Recall that K_1 will be 3.0 in the absence of an equilibrium isotope effect.)

Intermolecular Hydride Exchange. The rate constant k_{HH} for the associative exchange of hydrides with Cp_2WH_2 decreases substantially from $CpW(CO)_3H$ to $Os(CO)_4H_2$, $Cp_2W(H)CH_3$, and $Cp_2W(H)Ph$. As $CpW(CO)_3H$ is much more acidic[36] than the other hydrides, the fast H/D exchange between $CpW(CO)_3H$ and Cp_2WD_2 probably involves initial H$^+$ transfer. The other exchanges probably require hydridic character on the part of both partners. A reasonable mechanism is the four-centered one shown in eq 38 (although it is surprising to find an associative transition state for complexes that are coordinatively saturated and sterically crowded). One would expect steric crowding to inhibit this process, and indeed Parkin and Bercaw have recently found that intermolecular hydride exchange does not occur in $Cp^*{}_2W(H)CH_3$.[13]



(38)

It is clear that there is facile hydride exchange between Cp_2WH_2 and $Cp_2W(H)CH_3$. It seems highly probable that direct hydride exchange between different molecules of $Cp_2W(H)CH_3$ is facile and that such exchange is part of the global H/D scrambling we have observed at high concentrations. However, even if the rate constant for direct $Cp_2W(H)CH_3/Cp_2W(H)CH_3$ exchange were substantially lower than the $Cp_2WH_2/Cp_2W(H)CH_3$ rate constant, $Cp_2W(H)CH_3/Cp_2W(H)CH_3$ hydride exchange would still occur *indirectly* in the systems we have studied; our preparations of $Cp_2W(H)CH_3$ have always contained a few percent of Cp_2WH_2, which would catalyze hydride exchange among molecules of $Cp_2W(H)CH_3$ via successive exchanges between a molecule of Cp_2WH_2 and different molecules of $Cp_2W(H)CH_3$.

Concentration Dependence of Global Scrambling. We can now see how intermolecular hydride exchange permits global scrambling to occur at high concentrations and not at low ones. It is convenient to compare rates at 45 °C, a temperature at which all of the relevant rate constants are either known or can be estimated by extrapolation. At all concentrations, intramolecular

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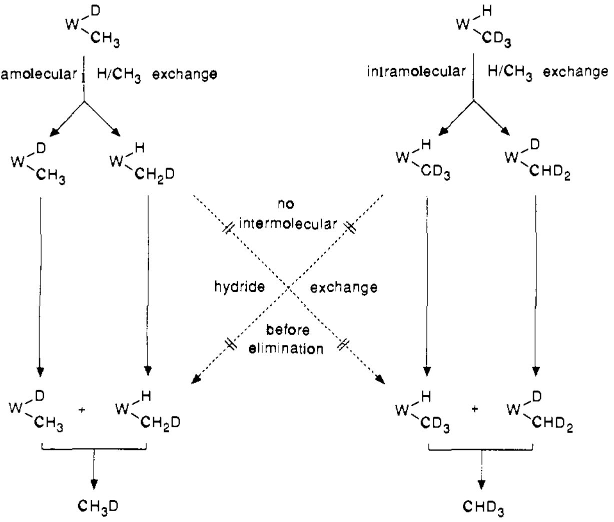
(34) (a) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225. (b) Ritchie, C. D. *Physical Organic Chemistry: The Fundamental Concepts*; Marcel Dekker: New York, 1975; Chapter 8. (c) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper: New York, 1987; p 255.

(35) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (b) Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111. (c) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969. (d) Dutta, T. K.; Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1987**, *6*, 842. A number of earlier examples are listed in footnote 15 of our communication.[11]

(36) The pK_a values of $CpW(CO)_3H$ and $Os(CO)_4H_2$ have been measured in CH_3CN, whereas Cp_2W hydrides are less acidic than solvent CH_3CN: Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

Scheme I. At Low Concentrations, H/CH_3 Exchange > CH_4 Elimination > Intermolecular H^- Exchange



exchange of methyl and hydride ligand hydrogens occurs with a rate constant of 2.5×10^{-5} s^{-1}, while reductive elimination of methane occurs more slowly, with a rate constant of 2.0×10^{-6} s^{-1}. Let us assume that the effective rate constant for $Cp_2W(H)CH_3/Cp_2W(H)CH_3$ hydride exchange, by the direct and the Cp_2WH_2-catalyzed paths combined, is about 5×10^{-4} M^{-1} s^{-1} (the approximate rate constant for $Cp_2WH_2/Cp_2W(H)CH_3$ hydride exchange). At the low concentrations (0.67 mM in $Cp_2W(D)CH_3$ and 0.67 mM in $Cp_2W(H)CD_3$) at which we observed thermal methane elimination to be intramolecular (reaction 11), the version of the McKay equation[33] in eq 39 gives 6.7×10^{-7} as $k_{H/D\,equil}$,

$$k_{H/D\,equil} = ([Cp_2W(D)CH_3]_{t=0} + [Cp_2W(H)CH_3]_{t=0})(5 \times 10^{-4}\ M^{-1}\ s^{-1}) \tag{39}$$

$$k_{intermol\ hydride\ equil} = ([Cp_2W(H)^{13}CH_3]_{t=0} + [Cp_2W(H)CD_3]_{t=0})(5 \times 10^{-4}\ M^{-1}\ s^{-1}) \tag{40}$$

the first-order rate constant for H/D equilibration between $Cp_2W(D)CH_3$ and $Cp_2W(H)CD_3$; as this rate constant is smaller than that for methane elimination, methane elimination occurs before intermolecular H/D exchange (Scheme I). At the higher concentrations (66 mM in $Cp_2W(H)^{13}CH_3$ and 132 mM in $Cp_2W(H)CD_3$) at which a single rate constant for global scrambling was observed ($k_C = k_H$ in reaction 16), eq 40 gives 10^{-4} s^{-1} as the first-order rate constant for intermolecular hydride exchange. The latter rate constant is not only larger than that for methane elimination but larger than that for intramolecular exchange of methyl and hydride ligand hydrogens, with the result that D rapidly spreads among all molecules in solution after it is transferred onto W from CD_3; i.e., intermolecular H/D scrambling processes operate much faster than intramolecular ones (Scheme II). At intermediate concentrations very complex kinetic behavior is predicted.

Reductive Elimination of Methane. Formation of a σ Complex as an Intermediate. When we put aside the distractions posed by global scrambling, the intramolecular process by which methane is eliminated from $Cp_2W(H)CH_3$ becomes straightforward. There are only two relevant results to be explained:

(1) Hydrogen scrambling between the methyl and hydride ligands of $Cp_2W(H)CH_3$ occurs more rapidly than methane elimination.

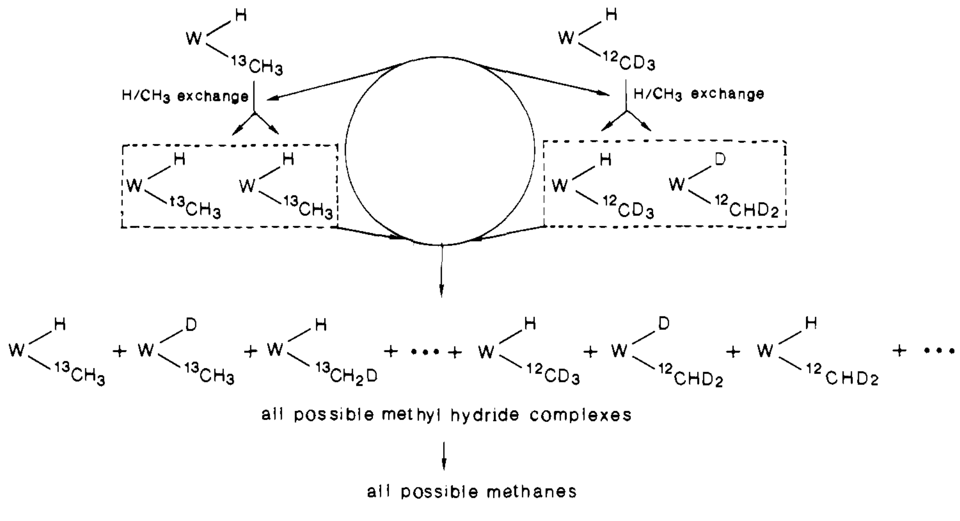
(2) Methane elimination shows an inverse isotope effect (i.e., the elimination of CD_4 from $Cp_2W(D)CD_3$ occurs more rapidly than the elimination of CH_4 from $Cp_2W(H)CH_3$).

The simplest comprehensive explanation for these facts parallels the interpretation offered by Bergman and co-workers for their observations on the elimination of cyclohexane from $Cp^*Ir(PMe_3)(H)Cy$[2b] and of R–H from $Cp^*Rh(PMe_3)(H)R$.[2d] In the iridium system, they suggested that elimination occurred through the reversible formation of a σ complex of cyclohexane, thus explaining (1) scrambling of D onto the α carbon of the cyclohexyl ligand prior to elimination from $Cp^*Ir(PMe_3)(D)Cy$ and (2) an inverse isotope effect when the rate of cyclohexane elimination from $Cp^*Ir(PMe_3)(H)Cy$ was compared with that of cyclohexane-d_{12} from $Cp^*Ir(PMe_3)(D)(Cy\text{-}d_{11})$. In the rhodium system, they suggested that R–H elimination occurred through the reversible formation of an R–H σ complex, thus explaining (1) scrambling of D onto the α, β, and γ carbons of various ligands R prior to elimination from $Cp^*Rh(PMe_3)(D)R$ and (2) an inverse isotope effect when the rate of ethane elimination from $Cp^*Rh(PMe_3)(H)C_2H_5$ was compared with that of ethane-d_6 from $Cp^*Rh(PMe_3)(D)C_2D_5$.

The formation of these σ complexes will lead to the observed patterns of deuterium scrambling if migration of the metal among the C–H bonds around a given carbon of the complex is more rapid than dissociation of the alkane. For example, migration of Ir from the C–D bond of $Cp^*Ir(PMe_3)(Cy\text{–}D)$ onto the C–H bond attached to the same carbon will lead to scrambling of D onto the α carbon of the cyclohexyl ligand when the cyclohexyl hydride complex is re-formed from the σ complex. Migration of Rh from the C–D bond of $Cp^*Rh(PMe_3)(R\text{–}D)$ onto the appropriate C–H bond of the R–D ligand will lead to scrambling of D onto the α, β, or γ carbon of R when the alkyl hydride complex is re-formed from the σ complex.

The formation of these σ complexes also explains the inverse isotope effects in a straightforward way. Although it is theoretically possible for a single-step process to have an inverse kinetic isotope effect, an observed inverse kinetic isotope effect usually

Scheme II. At High Concentrations, Intermolecular H^- Exchange > H/CH_2 Exchange > CH_4 Elimination



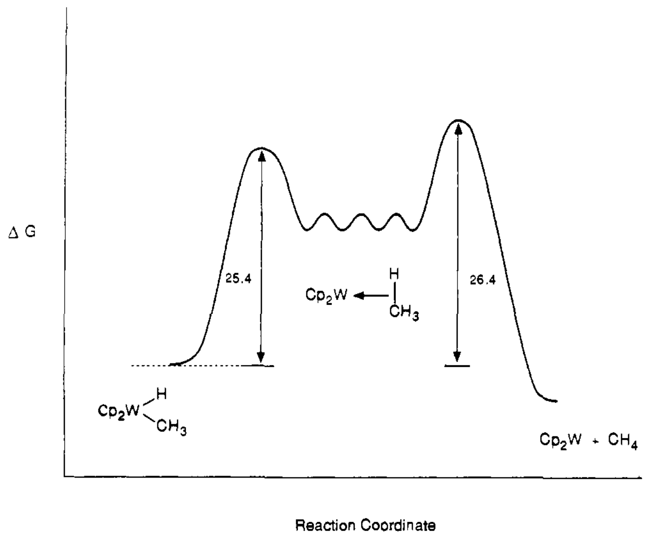
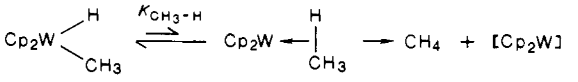
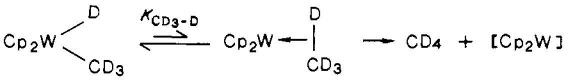


Figure 1. Free energy profile for the elimination of methane from $Cp_2W(H)CH_3$, with $\Delta G^{\ddagger}$ values in kilocalories per mole at 45 °C (assuming that W migration among the C–H bonds of the σ complex is rapid).

results from the operation of a multistep mechanism containing a preequilibrium with an inverse *equilibrium* isotope effect.[37] The formation of a cyclohexane σ complex in a preequilibrium from $Cp^*Ir(PMe_3)(H)Cy$ or $Cp^*Ir(PMe_3)(D)(Cy\text{-}d_{11})$ is accompanied by an inverse equilibrium isotope effect, because an Ir–H bond is replaced by a stronger C–H bond; the fraction of the Ir(D)Cy complex converted to the Cy–D σ complex by the preequilibrium is greater than the fraction of the Ir(H)Cy complex converted to the Cy–H σ complex.[2b] For the same reasons, the formation of an R–H σ complex in the rhodium system is accompanied by an inverse equilibrium isotope effect.[2d]

We believe that the reductive elimination of methane from $Cp_2W(H)CH_3$ proceeds through the reversible formation of a methane σ complex, as shown in eq 41 and 42 and in Figure 1.


(41)

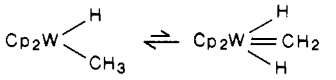

(42)

Rapid migration of the W from one methane C–H bond to another within the σ complex explains how hydrogen can scramble between the methyl and hydride ligands of $Cp_2W(H)CH_3$. A similar rearrangement in $Cp^*Rh(PMe_3)(H)CH_3$ has been suggested[35a] as an explanation for the failure of attempts to synthesize isotopically pure $Cp^*Rh(PMe_3)(D)CH_3$.

The analogy between a CH_4 σ complex and a side-on BH_4^- complex[38] and the fact that the bridging and terminal hydrogens of almost all BH_4^- complexes exchange rapidly on the NMR time scale[39] suggest that W migration among the C–H bonds of our σ complex will in fact be rapid. The observed barrier to hydrogen scrambling between the methyl and hydride ligands of $Cp_2W(H)CH_3$, 25.4 kcal/mol, is thus shown in Figure 1 as the barrier to σ complex formation. However, we have no experimental evidence to preclude the possibility that (1) σ complex formation from $Cp_2W(H)CH_3$ is rapid and reversible and (2) W migration from one C–H bond of the σ complex to another is the rate-determining step in hydrogen scrambling between the methyl and hydride ligands of $Cp_2W(H)CH_3$.

The formation of a methane σ complex in a preequilibrium from $Cp_2W(H)CH_3$ will be accompanied by an inverse equilibrium isotope effect, because a W–H bond is replaced by a stronger C–H bond, and thus $K_{CD_3\text{-}D}$ in eq 42 will be greater than $K_{CH_3\text{-}H}$ in eq 41. The isotope effect on loss of alkane from these σ complexes is probably small (because the C–H bond has already been formed in the σ complex); when it is combined with the inverse equilibrium isotope effect for the formation of the σ complexes, we obtain an inverse isotope effect ($k_{CH_3\text{-}H}/k_{CD_3\text{-}D} < 1.0$ in eq 31 and 32) for methane elimination. A similar inverse isotope effect has been observed, and a similar methane σ complex proposed as an intermediate, for the elimination of methane from $Cp^*_2W(H)CH_3$.[13]

It is possible to explain hydrogen scrambling between the hydride and methyl ligands of $Cp_2W(H)CH_3$ in other ways, such as the α elimination process in eq 43. However, such a process would be irrelevant to methane elimination and therefore would require an *independent* explanation for the observed inverse isotope effect. (Recall that an inverse isotope effect is unlikely[37] if methane elimination occurs in a single step.) The mechanism illustrated in eq 41 and 42 and in Figure 1 offers a much more straightforward explanation of both relevant results.


(43)

Our conclusion that a methane σ complex is formed in a preequilibrium from $Cp_2W(H)CH_3$ suggested the possibility of associative exchange of methane into that σ complex. We therefore checked for the incorporation of external methane into $Cp_2W(H)CH_3$ prior to elimination. However, ^1H NMR did not show the development of a methyl or hydride resonance when $Cp_2W(D)CD_3$ was heated under 70 psi of methane for 49 h (several half-lives for intramolecular exchange between the CD_3 and D ligands) at 42 °C.

Just as η^2-H_2 complexes play a major role in the elimination and addition of H_2,[40] it is increasingly clear that hydrocarbon σ complexes play a major role in the reductive elimination of alkanes from alkyl hydride complexes and therefore in the reverse process, hydrocarbon activation.[41-44] Brookhart, Green, and Wong, who have recently noted the analogy between hydrocarbon σ complexes and η^2-H_2 complexes, have stated that "the intermediacy of alkane–metal complexes...in the process of oxidative addition of a C–H bond to a transition-metal center is likely to be a quite normal occurrence" and have predicted the isolation of η^2-CH_4 complexes.[44]

Experimental Section

General Procedures. All experiments were performed under nitrogen using standard Schlenk, vacuum-line, or inert-atmosphere box techniques as indicated. Diethyl ether, hexane, THF, benzene, and toluene were distilled from sodium or potassium benzophenone ketyl. Cyclohexane, dichloromethane, acetonitrile-d_3, and benzene-d_6 were purified by vacuum transfer from P_4O_{10}. Water was distilled from chromous sulfate. PMDT was distilled from BaO by bulb-to-bulb vacuum distillation using a Kugelrohr apparatus. 2-Methoxyethanol was distilled from sodium. All other solvents and reagents were used without purification but were deoxygenated either by freeze–pump–thaw degassing or by prolonged N_2 purging. Cp_2WH_2,[45] Cp_2WCl_2,[46] $Cp_2W(CH_3)_2$,[46] $Cp_2W(CH_3)(OC(O)$-

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[37] Melander has said that "a very product-like transition state could give rise to an inverse kinetic isotope effect provided that the equilibrium effect is sufficiently strong and in the proper direction. In general this would require that a strongly endothermic reaction leads to a product in which the frequencies concerned with the atom transferred are higher than those of the reactant": Melander, L. *Acta Chem. Scand.* **1971**, *25*, 3821. However, as Bergman and co-workers have argued at length (footnote 25 in ref 2b and footnotes 14 and 15 in ref 2d), there are few if any cases in which observed inverse isotope effects cannot be attributed to preequilibria; single-step R–H eliminations appear to result in normal isotope effects (e.g., 3.3 from $PtH(CH_3)(PPh_3)_2$ vs $PtD(CH_3)(PPh_3)_2{}^6$).

[38] Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977.

[39] Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

[40] Kubas, G. *Acc. Chem. Res.* **1988**, *21*, 120, and references therein.

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[42] Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

[43] Low, J. J.; Goddard, W. A., III *Organometallics* **1986**, *5*, 609, and references therein.

[44] Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.

[45] Green, M. L. H.; Knowles, P. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 989–991.

Ph),[9a] and $Cp_2W(CH_3)H$[9a] were prepared by the methods of Green et al.

^1H NMR spectra were obtained using either a JEOL FX-100Q or an IBM WP-270 or WP-200 spectrometer. ^2H NMR spectra were obtained on a Nicolet 360-MHz spectrometer at the Colorado State University Regional NMR Center. Mass spectra were obtained on a VG MM-16F.

CD_3MgBr. CD_3Br (1.15 g, 11.7 mmol) was condensed into a 25-mL vacuum-line bulb. A dry ice/acetone condenser and a 100-mL Schlenk flask containing Reade high-purity magnesium turnings (218 mg, 8.97 mmol) were connected directly to a high-vacuum line through the side arm near the base of the condenser. The apparatus was evacuated and diethyl ether (~25 mL) was transferred into the reaction flask and freeze-pump-thaw degassed. Before the final thawing the condenser was charged with dry ice/acetone and an aliquot of CD_3Br was condensed into the reaction flask. The reaction mixture was allowed to warm slowly to room temperature; stirring was started after bubbling showed that the reaction had been initiated. The rest of the CD_3Br was added in aliquots (using a mercury manometer to control the addition) at a rate that maintained gentle reflux of the solution without external heating. After the addition was complete, the reaction was stirred until all of the magnesium was consumed (~1 h). The diethyl ether and excess CD_3Br were removed under reduced pressure to yield a white crystalline product, which was dried under vacuum for 1 h. The product was extracted with diethyl ether (35 mL) and filtered through a glass frit to give a clear, colorless solution (~0.36 M), which was stored under nitrogen. The exact concentration of the methyl magnesium bromide solution was not determined.

$Cp_2W(CD_3)_2$ was prepared by the method used by Benfield and Green[46] for $Cp_2W(CH_3)_2$. Solid Cp_2WCl_2 (0.75 g, 1.95 mmol) was added in small quantities over a period of 15 min to a vigorously stirred solution of CD_3MgBr (25 mL, ~0.36 M in diethyl ether, ~9.0 mmol). After 5 h the dark green suspension had changed into a red solution. The solvent was removed under vacuum and the residue cooled in liquid N_2. Ethanol (8 mL) was added slowly and the mixture allowed to warm to room temperature. The ethanol was then removed, and toluene (20 mL) and water (10 mL) were added to give a two-phase system, which was shaken vigorously. The emulsion that formed was filtered through a 1.5-cm Celite bed, and the toluene solution was separated from the aqueous phase. Removal of the toluene gave an oily red solid, which was extracted with hexane (2 × 10 mL). Removal of the hexane afforded a red solid, which was sublimed at 120 °C (10^{-3} Torr) to yield waxy red solid $Cp_2W(CD_3)_2$ (392 mg, 58%). IR (Nujol): ν_{C-D} 2175, 2090, 2040 cm^{-1}. ^1H NMR: δ 4.02 (C_6D_6).

$Cp_2W(CD_3)(OC(O)Ph)$ was prepared by the method used by Green and co-workers for $Cp_2W(CH_3)(OC(O)Ph)$.[9a] Benzoic acid (52 mg, 0.43 mmol) was added to a suspension of $Cp_2W(CD_3)_2$ (0.15 g, 0.43 mmol) in heptane (10 mL), and the mixture was heated at 60 °C for 1 h. Concentration of the resulting dark red solution yielded orange-red needles, which were collected and washed with cold heptane (2 × 1 mL) (155 mg, 80%).

$Cp_2W(H)CD_3$ was prepared by a modification of the method used by Cooper, Green, and Mahtab for $Cp_2W(H)CH_3$.[9a] A solution of $Cp_2W(CD_3)(OC(O)Ph)$ (155 mg, 0.34 mmol) in toluene (15 mL) was treated with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (0.87 mL, 3.46 M in benzene, 3.01 mmol). The dark red solution was stirred for 3 h to give a yellow-orange solution. Water (1 mL) was added dropwise very slowly with stirring. After hydrogen evolution had ceased, another 10 mL of water was added and the mixture stirred for 10 min. The clear yellow-orange toluene layer was separated and washed with water (2 × 10 mL). The toluene was removed under reduced pressure at 30 °C to give a bright yellow solid, which was dried under vacuum at room temperature for 15 h to remove the last traces of water. Sublimation at 50 °C (10^{-3} Torr) gave a yellow-orange solid (70 mg, 61%). IR (Nujol): (ν_{C-D}) 2180 m, 2090 m, 2045 m cm^{-1}; (ν_{W-H}) 1870 cm^{-1}. ^1H NMR (C_6D_6): δ 4.17 (Cp), −10.58 (W-H, J = 81 Hz).

$Cp_2W(^{13}CH_3)_2$. $^{13}CH_3MgBr$ was prepared from $^{13}CH_3Br$ (0.560 g, 5.84×10^{-3} mol) and Mg (0.118 g, 4.86×10^{-3} mol) in Et_2O by the procedure described above for CD_3MgBr. Cp_2WCl_2 (0.415 g, 1.08×10^{-3} mol) was added, and the mixture was stirred overnight. The product was isolated using the procedure described above for $Cp_2W(CD_3)_2$, except that the toluene/water emulsion was not filtered. Yield: 0.178 g, 48%. ^1H NMR (C_6D_6): δ 4.01 (Cp), 0.25 (m, $^1J_{C-H} \approx 127$ Hz, $^{13}CH_3$ of $Cp_2W(^{13}CH_3)_2$), 0.25 (d, $^3J_{C-H}$ = 2.6 Hz, $^{12}CH_3$ of $Cp_2W(^{12}CH_3)^{13}CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −24.5 (J_{W-C} = 68.4 Hz).

$Cp_2W(H)^{13}CH_3$. $PhCO_2H$ (0.048 g, 3.93×10^{-4} mol, 0.98 equiv) was added as a solid to a solution of $Cp_2W(^{13}CH_3)_2$ in hexane (15 mL). After heating at 60 °C for 1 h, the solvent was evaporated to give crude $Cp_2W(^{13}CH_3)OCOPh$ as a brown solid, which was not purified. Addition of toluene (15 mL) and an excess of $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ (1.0 mL of a 3.4 M solution in toluene) gave a red-brown solution, which turned to an orange-yellow color over 4 h. Water (10 mL) was added slowly, and the toluene layer was separated and washed with water (3 × 10 mL). The toluene was evaporated, and the product was dried under vacuum overnight. Sublimation at 45 °C gave $Cp_2W(H)^{13}CH_3$ as a yellow solid (0.078 g, 60% based on $Cp_2W(^{13}CH_3)_2$). ^1H NMR (C_6D_6, 200 MHz): δ 4.16 (Cp), 0.02 (dd, $^1J_{C-H}$ = 125 Hz, $^3J_{H-H}$ = 0.9 Hz, $^{13}CH_3$), −10.58 (d, $^2J_{C-H}$ = 7.8 Hz, $^1J_{W-H}$ = 81 Hz). Also observed in the ^1H NMR: $^{12}CH_3$ resonance due to $Cp_2W(H)^{12}CH_3$ at δ 0.02 ($^3J_{H-H}$ = 0.9 Hz), hydride peak at δ −12.26 due to Cp_2WH_2 (about 3% impurity).

Determination of Active Hydride in $LiAlH_4$ (or $LiAlD_4$). The hydride activity of $LiAlH_4$ and $LiAlD_4$ samples was determined by iodimetric methods. In a typical analysis $LiAlH_4$ (100 mg, 2.64 mmol) was dissolved in THF (20 mL) and the solution filtered if necessary to give a clear solution. This solution was vigorously stirred and treated with a solution of iodine (1.465 g, 5.77 mmol) in THF (25 mL). After hydrogen evolution had ceased the excess iodine was titrated with a standardized sodium thiosulfate solution using starch as an indicator.

$Li[AlD_2(OCH_2CH_2OCH_3)_2]$. A suspension of $LiAlD_4$ (0.153 g, active deuteride 3.61 mmol) in THF (20 mL) was stirred for 16 h to effect dissolution. The small amount of undissolved solids was removed by filtration. The resulting clear solution was cooled to 0 °C and vigorously stirred as 2-methoxyethanol (0.57 mL, 7.23 mmol) was slowly added dropwise over a period of 10 min. The solution was stirred at 0 °C for a further 10 min and then allowed to warm slowly to room temperature. The solvent was removed under reduced pressure, and the resulting viscous residue was pumped on for 1 h. Extraction with benzene (5 mL) gave an almost clear solution of $Li[AlD_2(OCH_2CH_2OCH_3)_2]$ (~0.72 M), which was used without further purification.

$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4D)W(CH_3)H$. A solution of $Cp_2W(CH_3)(OC(O)Ph)$ (265 mg, 0.59 mmol) in toluene (15 mL) was treated with $Li[AlD_2(OCH_2CH_2OCH_3)_2]$ (5 mL, 0.72 M in benzene, 3.61 mmol). The dark red solution was stirred for 4 h to give a yellow-orange solution. An aqueous workup as described above for $Cp_2W(H)CD_3$ afforded the product as a yellow-orange solid (120 mg, 62%) following sublimation [50 °C (10^{-3} Torr)]. IR (Nujol): 1875 cm^{-1} (s, ν_{W-H}). ^1H NMR (C_6D_6): δ 4.16 (s, Cp), 0.02 (s, CH_3), −10.58 (s, W-H). MS (*m/e*, rel intens, assignment) for ^{184}W: 331, 9, $[W(C_5H_5)(C_5H_4D)(CH_3)H]^+$; 315, 100, $[W(C_5H_5)(C_5H_4D)]^+$.

$[Cp_2WHLi]_4$. A solution of Cp_2WH_2 (0.5 g, 1.59 mmol) in toluene (60 mL) as treated with 1.54 M *n*-butyllithium (1.05 mL, 1.62 mmol). After 1–2 min the solution developed a slight cloudiness; glyme was then slowly added dropwise with stirring until the cloudiness dissipated (2–3 drops). The fine yellow crystalline product began to separate after 4–5 min. After 1.5 h the bright yellow crystals were collected, washed with toluene (2 × 5 mL), and dried under vacuum (0.45 g, 88%).

Isolation of $Cp_2WH(Li{\cdot}PMDT)$. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDT; 0.085 mL, 0.50 mmol) was added to a suspension of Cp_2WH_2 (0.15 g, 0.48 mmol) in hexane (20 mL). The suspension was cooled to −78 °C and treated with 1.54 M *n*-butyllithium (0.32 mL, 0.49 mmol). The stirred mixture was allowed to warm slowly to room temperature (~1 h). After filtration the orange solid was washed with hexane (5 mL) and dried under vacuum (0.18 g, 77%).

$Cp_2W(H)CH_3$ from Cp_2WH_2 and PMDT. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDT; 0.085 mL, 0.50 mmol) was added to a solution of Cp_2WH_2 (0.15 g, 0.48 mmol) in toluene (20 mL). The reaction was then cooled to −78 °C, and *n*-butyllithium (0.32 mL, 1.54 M in hexane, 0.49 mmol) was added; the mixture was stirred and allowed to warm slowly to room temperature (~1 h). The resulting orange solution was added dropwise (using a cannula and positive N_2 pressure) to a stirred solution of methyl tosylate (3.10 mL, 1.59 M in benzene, 4.93 mmol) in benzene (5 mL); stirring was continued for 10 min after the addition was completed. $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (1.40 mL, 3.46 M in benzene, 4.84 mmol) was then added slowly. After 5 min, water (1 mL) was cautiously added. The remainder of the workup was that described above for $Cp_2W(H)CD_3$, except that the crude product was dried under vacuum at room temperature for at least 48 h to remove the last traces of PMDT. Sublimation at 50 °C (10^{-3} Torr) for 4 h gave $Cp_2W(H)CH_3$ as a yellow-orange solid (100 mg, 64%).

$(\eta^5\text{-}C_5H_5)_2WD_2$.[21] $(\eta^5\text{-}C_5H_5)_2WH_2$ (0.20 g, 0.63 mmol) was placed in a flat-bottomed pressure-equalizing dropping funnel containing a spin bar. The apparatus was wrapped in a cloth containing dry ice. Deuterium chloride (5 mL, 2 M in D_2O, 10 mmol) was added and the resulting solution stirred for 5 min. Sodium deuteroxide (1 mL, 12 M in D_2O, 12 mmol) was added slowly and the suspension that formed was stirred for 5 min. Toluene (30 mL) was added, and the precipitate was extracted into the organic phase. The aqueous layer was discarded.

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(46) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324–1331. Benfield, F. W. S. Ph.D. Thesis, Oxford University, 1972.

Deuterium chloride (5 mL, as above) was added, and the two-phase system was vigorously stirred for 10 min to effect extraction into the aqueous phase. Sodium deuteroxide (1 mL, as above) was added slowly and the suspension that formed in the aqueous layer was rapidly extracted into the toluene layer. The toluene layer was separated from the aqueous phase. Removal of the toluene afforded yellow needles, which were dried under vacuum for 15 h and sublimed at 100 °C (10^{-3} Torr) to yield a pale yellow crystalline product (150 mg, 75%).

Reaction of Cp_2WD_2 with *n*-BuLi. A solution of Cp_2WD_2 (0.12 g, 0.38 mmol) in toluene (30 mL) at 65 °C was treated with *n*-butyllithium (0.26 mL, 1.54 M in hexane, 0.40 mmol), and the solution was allowed to cool slowly to room temperature (2.5 h). Yellow-orange crystals separated, which were collected, washed with toluene (2 × 2 mL), and dried under vacuum (103 mg, 85%). The IR spectrum showed ν_{W-H} bands at 1750 and 1710 (sh) cm^{-1}.

A sample of this product (10 mg) suspended in C_6D_6 (0.3 mL) in a sealed 5-mm NMR tube was treated with D_2O (0.05 mL) to afford a homogeneous solution. ^1H NMR showed a signal at δ −12.27 with a $J_{^{183}W-H}$ of 73.3 Hz.

$Cp_2W(D)CH_3$. A solution of $Cp_2W(CH_3)H$ (150 mg, 0.45 mmol) in benzene (15 mL) was treated with *n*-butyllithium (0.35 mL, 1.54 M in hexane, 0.54 mmol). After 3–4 min, glyme was added slowly dropwise with stirring until the solution developed a slight cloudiness (1–2 drops). The fine yellow crystalline product began to separate after 2–3 min, and the reaction was stirred for 1 h to give a yellow suspension. This suspension was added dropwise (using a cannula and positive N_2 pressure) to a vigorously stirred two-phase mixture of D_2O (2 mL) and benzene (10 mL). Stirring was continued for 5 min after the addition was completed. Removal of solvents afforded a yellow solid, which was dried under vacuum at room temperature for 15 h. Sublimation [45 °C (10^{-3} Torr)] for 4 h afforded a yellow-orange solid (115 mg, 76%). IR (Nujol): ν_{W-D} 1345 cm^{-1}. ^1H NMR (C_6D_6): δ 0.01 (s, $J_{^{183}W-^1H}$ = 5.8 Hz, with the J_{H-CH_3} = 1.2 Hz of $Cp_2W(H)CH_3$ absent).

$Cp_2W(D)CD_3$. A solution of $Cp_2W(CD_3)H$ (29 mg, 0.09 mmol) in benzene (5 mL) was treated with *n*-butyllithium (0.06 mL, 1.54 M in hexane, 0.09 mmol). The rest of the reaction procedure was the same as that for the preparation of $Cp_2W(CH_3)D$. Sublimation [45 °C (10^{-3} Torr)] for 4 h afforded a yellow-orange solid (17.5 mg, 60%). ^1H NMR (C_6D_6): δ 4.17 (s, Cp).

$Cp_2W(\eta^2\text{-}CH_3CN)$. A solution of $Cp_2W(H)CH_3$ (49 mg, 1.48×10^{-4} mol) in CH_3CN (31 mL) was heated at 79.8 °C for 11 h. Evaporation of solvent and sublimation of the residue at 90 °C gave $Cp_2W(\eta^2\text{-}CH_3CN)$ (25 mg, 7.04×10^{-5} mol, 48%) as an orange solid. ^1H NMR (C_6D_6): δ 4.12 (Cp), 2.58 (CH_3). MS: *m/e* 355 (^{184}W). Anal. Calcd for $C_{12}H_{13}NW$: C, 40.59; H, 3.69. Found: C, 40.44; H, 3.87.

Preliminary Kinetics of Thermolysis of $Cp_2W(H)CH_3$. A stock solution of $Cp_2W(CH_3)H$ (0.0047 g, 0.014 mmol) in C_6D_6 (2 mL), containing cyclohexane (0.25 mol equiv relative to $Cp_2W(CH_3)H$) as an internal standard, was prepared. Aliquots (0.15 mL) of the stock solution were pipetted into two 5-mm NMR tubes, which had been sealed onto vacuum-line adapters. C_6D_6 (0.24 mL) was added to one tube; C_6D_6 (0.20 mL) and CD_3CN (0.04 mL) were added to the second tube. The contents of the tubes were then degassed by three freeze-pump-thaw cycles, and the tubes were sealed under vacuum. These samples were stored at −10 °C prior to use.

The thermal decompositions were performed in constant temperature baths (±0.2 °C). Samples were removed from the baths at intervals and cooled to room temperature prior to analysis by ^1H NMR. The extent of decomposition was determined by comparing the peak height of the methyl ligand resonance of the starting material with that of the cyclohexane internal standard. The reactions were followed through at least 3 half-lives.

Determination of the Molecularity of the Thermal and Photochemical Elimination of Methane from Dilute Solutions of $Cp_2W(H)CH_3$. A solution that was 0.67 mM in $Cp_2W(H)CD_3$ and 0.67 mM in $Cp_2W(D)CH_3$ was prepared by combining $Cp_2W(H)CD_3$ (20 mg, 6.0×10^{-5} mol) and $Cp_2W(D)CH_3$ (20 mg, 6.0×10^{-5} mol) in 90 mL of 90% toluene/10% CH_3CN. The solution was heated at 82.5 °C for 6 h. The noncondensable gases were collected by Toepler pump, and the flask containing the gas sample was pressurized up to 1 atm with helium. The mass spectrum of the gas mixture was analyzed; peak heights in the *m/e* 12–20 range were measured (and corrected for background noise). The percentages of the five isotopically labeled methanes were obtained from METHNAL, a program that calculates these five unknowns from the nine observed intensities and the standard spectra[31] of CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 by overdetermined-least-squares methods.[47] The results are given in Table I.

The photochemical experiment was carried out by photolyzing another sample of the same solution in a quartz tube for 6 h at <5 °C, using a 450-W Hanovia Hg lamp. The percentages of isotopically labeled methanes calculated by METHNAL are given in Table II.

The principal organometallic product observed by ^1H NMR from the thermal reaction was $Cp_2W(\eta^2\text{-}CH_3CN)$. The residue from the photochemical reaction was a dark brown solid of low solubility which was not identified.

A solution of $Cp_2W(H)(^{13}CH_3)$ (9 mg, 2.7×10^{-5} mol, 0.54 mM, 93% ^{13}C) and $Cp_2W(D)CD_3$ (9 mg, 2.7×10^{-5} mol, 0.54 mM, about 88% D on tungsten) in 50 mL of 90% benzene/10% CH_3CN was heated at 82.9 °C for 2.5 h. Collection of the noncondensable gas by Toepler pump gave 5.1×10^{-5} mol (95% yield of methanes). Overdetermined-least-squares analysis showed that the principal isotopically labeled methanes were $^{13}CH_4$ (40 ± 6%), CD_4 (42 ± 6%), and CHD_3 (14 ± 6%).

Global Scrambling. An NMR tube containing a C_6D_6 solution of $Cp_2W(H)^{13}CH_3$ (11.0 mg, 66 mM) and $Cp_2W(H)CD_3$ (22.0 mg, 132 mM) was sealed and placed in a constant temperature bath at 47.3 °C. At appropriate intervals the tube was removed, and ^{13}C and ^1H NMR spectra were recorded at ambient temperatue. The relative amounts of $Cp_2W(H)^{13}CH_3$ (δ −41.35, qd, $^1J_{C-H}$ = 125 Hz, $^2J_{C-H}$ = 7 Hz; compound A in eq 16) and $Cp_2W(H)^{13}CH_2D$ (δ −41.60, $^1J_{C-H}$ = 125 Hz, $^1J_{C-D}$ = 19 Hz, $^1J_{C-H}$ = 7 Hz; compound B in eq 16) were determined at each sampling time from ^{13}C NMR peak heights. (Data collection proved practical for only 1 half-life, during which time these two species were the only ones present in quantities high enough to be observable by ^{13}C NMR.) For each sampling time *t*, the fraction, C_t in eq 18, of all methyl signals that belonged to $^{13}CH_3$ was calculated; at the early reaction times at which data were collected, C_1 was effectively $A/(A + B)$.

Similarly, for each sampling time *t*, the fraction, H_1 in eq 19, of all methyl and hydride ^1H NMR signals that belonged to ^{12}C methyl groups ($^{12}CH_nD_{3-n}$) was calculated from the combined ^1H NMR integral of $^{12}CH_3$, $^{12}CH_2D$, and $^{12}CHD_2$ versus the combined ^1H NMR integral of all methyl and hydride signals. By the methods described in Appendix II C_∞ was calculated as 0.093 and H_∞ as 0.469. The rate constants k_C and k_H were then calculated from eq 22 and 23.

Similar crossover experiments employing $Cp_2W(H)^{13}CH_3/Cp_2W(D)CH_3$ and $Cp_2W(H)^{13}CH_3/Cp_2W(D)CD_3$ were also performed but were not analyzed in detail.

Determination of K_1(apparent) and K_2(apparent). A solution of $Cp_2W(H)CD_3$ in C_6D_6 (0.03–0.10 M) or $Cp_2W(D)CH_3$ in C_6H_6 (0.030 M) was sealed under vacuum in an NMR tube. The resulting sealed tube was placed in a constant temperature bath; it was removed at intervals and analyzed by ^1H NMR (for $Cp_2W(H)CD_3$) or ^2H NMR (for $Cp_2W(D)CH_3$), with the spectrometer held at 10–15 °C. After global H/D scrambling had proceeded for 8–10 half-lives, the relative integrals of the remaining methyl and hydride resonances were used to determine K_1(apparent) and K_2(apparent).

The K_1 results did not vary with temperature between 40 and 50 °C.

Determination of the Molecularity of the Thermal Elimination of Methane from Concentrated Solutions of $Cp_2W(H)CH_3$. A mixture of 3.6 mL of C_6H_6 and 0.4 mL of CH_3CN was degassed on a high-vacuum line and transferred into a 25-mL bulb containing 18.4 mg (0.056 mmol) of $Cp_2W(D)CH_3$ and 12.5 mg (0.0375 mmol) of $Cp_2W(H)CD_3$. The bulb was closed and heated to 81.6 °C for 179 min. The noncondensable gases were collected with a Toepler pump, and enough helium was added to raise the total pressure above 1 atm. Gas samples were then removed by syringe and injected into the mass spectrometer. The percentages of isotopically labeled methanes calculated by METHNAL from the intensities of the hydrocarbon fragments at *m/e* 12–20 were the following: CH_4, 9 (4); CH_3D, 17 (5); CH_2D_2, 24 (6); CHD_3, 35 (4); CD_4, 15 (4).

Intermolecular Exchange between $Cp_2W(H)CH_3$ and Other Hydrides. When a C_6D_6 solution of $Cp_2W(H)CH_3$ (20 mM) and Cp_2WD_2 (14 mM, 95% D by ^1H NMR) was heated to 45 °C for 2 h, the hydride resonance of the dihydride increased with concomitant decrease of the hydride resonance of $Cp_2W(H)CH_3$. Similarly, when a C_6H_6 solution of $Cp_2W(D)CD_3$ (133 mM, 95% D in hydride) and Cp_2WH_2 was heated to 47 °C for 5 h, the ^2H resonance of $Cp_2W(D)CD_3$ decreased while a signal due to ^2H on W in the dihydride appeared. Additional solutions containing $Cp_2W(H)CH_3$ and Cp_2WD_2 at the concentrations shown in Table III were then prepared; 0.55 mL of a 90:10 mixture of toluene-d_8 and CD_3CN and 2–3 μL of dodecane as internal standard were added to NMR tubes containing appropriate amounts of these compounds, and the tubes were then sealed under vacuum. The concentrations of the reactants at infinite time were calculated using the known initial concentrations and the assumption that there was no isotope effect on the equilibrium constant. The reactions were run at 48.2 °C and monitored by removing each sealed tube from the constant temperature bath at appropriate intervals and taking its ^1H NMR spectrum at −30 °C. Following either the increase in the integral of the hydride resonance of the

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(47) Brauman, J. *Anal. Chem.* **1966**, *38*, 607.

dihydride or the decrease in the integral of the hydride resonance of $Cp_2W(H)CH_3$ yielded first-order rate constants for approach to isotopic equilibrium (Table III) that were identical within experimental error.

The rate constants for intermolecular hydride exchange between Cp_2WD_2 and other hydride complexes at 50 °C were determined in the same way. The hydrides used, and the measured first-order rate constants for approach to isotopic equilibrium, were the following: Cp_2WD_2, $Cp_2W(H)Ph$, $4.4 \times 10^{-5}\ s^{-1}$; Cp_2WD_2, $CpW(CO)_3H$, $10^{-2}\ s^{-1}$; Cp_2WD_2, $Os(CO)_4H_2$, $1.74 \times 10^{-4}\ s^{-1}$.

Intramolecular Exchange of Hydrogen between the Methyl and Hydride Ligands of $Cp_2W(H)CH_3$. An NMR tube was sealed under vacuum with a 0.7 mM solution of $Cp_2W(D)CH_3$ (hydride ligand 95% D) in 90:10 toluene-d_8/CD_3CN, without an internal standard. The tube was placed in a constant temperature bath at 48 °C. Its approach to isotopic equilibrium was monitored by removing the tube at appropriate intervals and taking its ^1H NMR spectrum. The methyl and hydride resonances were integrated relative to each other and used to calculate the extent of reaction (from eq 28) as a function of time. The extent of reaction at infinite time was calculated from K_1(apparent) and used to calculate the first-order rate constant for approach to isotopic equilibrium.

Kinetics of the Thermolysis of $Cp_2W(H)CH_3$ and $Cp_2W(D)CD_3$. Stock solutions of the tungsten complexes ($\sim 6.5 \times 10^{-2}$ M) in benzene-d_6 (1 mL) containing cyclohexane (0.25 mol equiv relative to the tungsten complexes) as an internal standard were prepared. Aliquots (0.15 mL) of the stock solution were pipetted into 5-mm NMR tubes. Benzene-d_6 (0.20 mL) and acetonitrile-d_3 (0.04 mL) were added to each tube. The contents of the tubes were then degassed by three freeze-pump-thaw cycles, and the tubes were sealed under vacuum.

The thermal decompositions were performed in constant temperature baths (±0.2 °C). Samples were removed from the baths at intervals and cooled to room temperature prior to analysis by NMR. Spectra were taken to cover 2-3 half-lives of the reaction, with approximately 3-5 points/half-life. The rate constants in Table IV for the elimination of methane from $Cp_2W(H)CH_3$ were determined by ^1H NMR as follows: at 80.5 °C, the integrals of both the hydride (δ −10.57) and the methyl peak (δ 0.03) vs the internal standard cyclohexane were measured for each point; at the other temperatures, the height of the methyl resonance was compared with that of the cyclohexane internal standard.

The kinetic isotope effect for the elimination of CH_4 from $Cp_2W(H)CH_3$ vs the elimination of CD_4 from $Cp_2W(D)CD_3$ was obtained by comparing the rates at which the two elimination reactions occurred at 72.6 °C in separate sealed tubes containing pure CD_3CN as solvent. Concentrations of 77 mM ($Cp_2W(H)CH_3$) and 67 mM ($Cp_2W(D)CD_3$) were employed, with neopentane included as the internal standard; the hydride ligand of the $Cp_2W(D)CD_3$ was 95% deuterated, and the methyl ligand was >97% deuterated. The progress of the elimination reactions was monitored by removing each sealed tube from the constant temperature bath at appropriate intervals and taking its ^1H NMR spectrum at 10 °C. Delays between pulses of 5 times the longest ^1H T_1 were used in obtaining the spectra, and the cyclopentadienyl resonance of $Cp_2W(H)CH_3$ or $Cp_2W(D)CD_3$ was integrated vs that of the neopentane. The same kinetic isotope effect was obtained at 80.5 °C by using ^2H NMR to monitor the rate of CD_4 elimination from $Cp_2W(D)CD_3$ and comparing that result with the $Cp_2W(H)CH_3$ one in Table IV.

Lack of Exchange between $Cp_2W(D)CD_3$ and External CH_4. $Cp_2W(D)CD_3$ (27 mg, hydride ligand 90% D) was dissolved in 0.5 mL of CD_3CN and stirred under 70 psi of CH_4 for 49 h at 42 °C. ^1H NMR showed no incorporation of the CH_4 into the $Cp_2W(D)CD_3$.

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Appendix I. Relationships between Observed Intensity Ratios, Mole Fractions of D in Various Locations, and K_1

Let y = mole fraction of D in methyl group, z = mole fraction of D in hydride site, and f = mole fraction of D in the entire system (methyl and hydride sites combined).

Let K_1 be the equilibrium constant for eq 14. In view of the statistical weight of the methyl and hydride sites

$$(3y + z)/4 = f \tag{A1}$$

If we define K_1(apparent) as (intensity of ^1H methyl resonance)/(intensity of ^1H hydride resonance), then

$$\frac{1}{K_1(\text{apparent})} = (1 - z)/[1(\text{fraction } CHD_2) + 2(\text{fraction } CH_2D) + 3(\text{fraction } CH_3)] \tag{A2}$$

$$= \frac{1 - z}{3y^2(1 - y) + 6y(1 - y)^2 + 3(1 - y)^3} \tag{A3}$$

After using eq A1 to write z in terms of f and y and simplifying, we obtain

$$\frac{1}{K_1(\text{apparent})} = \frac{1 - 4f + 3y}{3 - 3y} \tag{A4}$$

Similarly, if we define K_2(apparent) as (intensity of ^2H methyl resonance)/(intensity of ^2H hydride resonance), then

$$\frac{1}{K_2(\text{apparent})} = z/[3(\text{fraction } CD_3) + 2(\text{fraction } CD_2H) + 1(\text{fraction } CDH_2)] \tag{A5}$$

$$= \frac{z}{3y^3 + 6y^2(1 - y) + 3y(1 - y)^2} \tag{A6}$$

After using eq A1 to write z in terms of f and y and simplifying, we obtain

$$\frac{1}{K_2(\text{apparent})} = \frac{4f - 3y}{3y} \tag{A7}$$

If we now express the mole fractions of $Cp_2W(H)CD_3$ and $Cp_2W(D)CHD_2$ in terms of y and z, the mole fraction of $Cp_2W(H)CD_3$ is $y^3(1 - z)$ and the mole fraction of $Cp_2W(D)CHD_2$ is $3y^2(1 - y)z$. Thus

$$K_1 = \frac{3y^2(1 - y)z}{y^3(1 - z)} \tag{A8}$$

Using eq A1 to write z in terms of f and y again and simplifying gives

$$K_1 = \frac{3(4f - 4fy - 3y + 3y^2)}{y(1 - 4f + 3y)} \tag{A9}$$

With $Cp_2W(H)CH_3$ as a starting material, and f therefore equal to 0.75, K_1(apparent) was measured as 1.6 after complete H/D scrambling at 45.0 °C; eq A4 gave 0.795 for the value of y. With $Cp_2W(D)CH_3$ as a starting material, and f therefore equal to 0.25, K_2(apparent) was measured as 4.9 after complete H/D scrambling at 45.0 °C; eq A7 gave 0.277 for the value of y. Substitution into eq A9 of the combinations of y and f from both the experiment starting with $Cp_2W(H)CD_3$ and the experiment starting with $Cp_2W(D)CH_3$ gave the true value of K_1 as 1.4 (2).

Appendix II. C_∞ and H_∞ as a Function of K_1 and the Mole Fraction of D

Equation A9 implicity gives y as a function of K_1 and f. Then, from the definitions of C_t and of y

$$C_\infty = (1 - y)^3 \tag{A10}$$

In order to calculate H_∞, we define x as the mole fraction of ^{13}C in methyl ligand carbons. Then the intensity of the $^{12}CH_nD_{3-n}$ ^1H NMR signal is proportional to $(1 - x)[1(\text{fraction } CD_2H) + 2(\text{fraction } CDH_2) + 3(\text{fraction } CH_3)]$. Similarly, the intensity of the $^{13}CH_nD_{3-n}$ ^1H NMR signal is proportional to $x[1(\text{fraction } CD_2H) + 2(\text{fraction } CDH_2) + 3(\text{fraction } CH_3)]$ and the intensity of the hydride signal is proportional to $(1 - z)$.

Thus, from the definition of H_1, H_∞ is given by

$$H_\infty = \frac{(1-x)[1(\text{fraction}CD_2H)+2(\text{fraction}CDH_2)+3(\text{fraction}CH_3)]}{[1(\text{fraction}CD_2H)+2(\text{fraction}CDH_2)+3(\text{fraction}CH_3)]+(1-z)} \tag{A11}$$

Substitution (as in eq A3) and simplification (as in eq A4) gives

$$H_\infty = \frac{(1 - x)(3 - 3y)}{4 - 3y - z} \qquad \text{(A12)}$$

Use of the value of f (0.50) established at the beginning of the $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ experiment with K_1 in eq A9 gave the value of y to be expected at the end of that experiment; eq A1 gave the expected value of z, and eq A10 and A12 gave the expected values of C_∞ and H_∞.

Registry No. CD_3MgBr, 77491-27-1; CD_3Br, 1111-88-2; Cp_2WCl_2, 12184-26-8; $Cp_2W(CD_3)_2$, 119908-43-9; $Cp_2W(CD_3)(OC(O)Ph)$, 119908-44-0; $Cp_2W(H)CD_3$, 94370-31-7; $Cp_2W(CH_3)(OC(O)Ph)$, 73210-66-9; $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4D)W(CH_3)H$, 94370-29-3; $Cp_2W(^{13}CH_3)_2$, 119908-45-1; $^{13}CH_3Br$, 51624-21-6; $[Cp_2WHLi]^4$, 53322-18-2; Cp_2WHz, 1271-33-6; $Cp_2WH(Li{\cdot}PMDT)$, 119908-47-3; $Cp_2W(H)CH_3$, 72415-89-5; $(\eta^5\text{-}C_5H_5)_2WD_2$, 11082-26-1; $Cp_2W(D)CH_3$, 94370-30-6; $Cp_2W(D)CD_3$, 94370-33-9; $Cp_2W(\eta^2\text{-}CH_3CN)$, 119908-48-4; $Cp_2W(H)Ph$, 11077-71-7; $Cp_2W(CO)_3H$, 12128-26-6; $Os(CO)_4H_2$, 22372-70-9; D_2, 7782-39-0; $Cp_2W(H)^{13}CH_3$, 94370-32-8; $Li[AlD_2(OCH_2CH_2OCH_3)_2]$, 119908-49-5.

Intramolecular Coupling between Tricarbonyl(diene)iron Complexes and Pendant Alkenes

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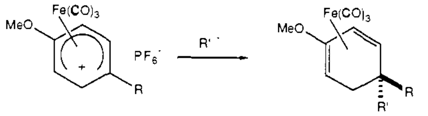
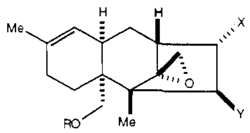
Abstract: New methodology for carbon–carbon bond formation, suitable for the construction of quaternary carbon centers, is described. The procedure involves the intramolecular reaction of an alkene with a cyclohexadiene–$Fe(CO)_3$ complex at elevated temperature (140 °C), resulting in the formation of spirolactones and spirolactams. The simple example is conversion of tricarbonyl(allyl 1–4-η-cyclohexa-1,3-dienecarboxylate)iron (**24a**) to tricarbonyl(6–9-η-1-oxo-4-methyl-2-oxaspiro[4.5]-deca-6,8-diene)iron (**25a**). A fairly extensive study of the scope of the reaction is reported, and it is shown that cyclopentenes will couple with the cyclohexadiene–$Fe(CO)_3$, giving tricyclic intermediates of potential value for the synthesis of trichothecene derivatives. Methods for controlling the stereochemical outcome of the reaction, by suppressing pre- and postcyclization rearrangement of the diene–$Fe(CO)_3$ moiety, are described. A discussion of the mechanism of the coupling reaction, which involves prior dissociation of CO ligand from the organometallic group, is presented.

The studies described in this paper were undertaken in an attempt to overcome a number of shortcomings in the use of (cyclohexadienyl)iron complexes for the construction of sterically congested quaternary carbon centers. For several years we have been exploring the reactions of carbon nucleophiles with dienyl complexes of general structure **1**, in which electronic deactivation of C(5) by the 4-methoxy group directs nucleophile addition to C(1), giving products of structure **2**, even when this position is substituted.[1] This behavior has been exploited in the total synthesis of unnatural trichothecene analogues **3**[2] and **4**[3] and more recently in a short diastereoselective synthesis of trichodiene[4] (**5**), the biogenetic precursor of naturally occurring trichothecenes.[5] Because of the interesting biological activity of many of the trichothecenes (e.g., antibiotic, antitumor, and antifungal), especially those having hydroxyl functionality at C(15), exemplified by verrucarol (**6**) and calonectrin (**7**), we also investigated the generality of using complexes related to **1** as synthetic precursors for this family of natural products.

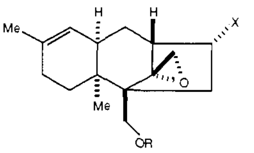


1

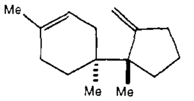
2



6 X = R = H, Y = OH
7 R = Ac, X = OAc, Y = H



3 X = H, R = Me
4 X = R = OH



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In order to generate intermediates of potential value for synthesis of **6** and **7**, we initially considered using dienyl-$Fe(CO)_3$ complexes **1** ($R = CH_2OP$) or **1** ($R = CO_2Me$). By analogy with the conversion of **1** (R = Me) to complexes **8** (used in the synthesis of **3** and **4**) and **9** (used as a precursor to **5**), we expected that various enolates of cyclopentanone would react with the requisite dienyl precursors to generate intermediates such as **10** or **11**. In view of the well-precedented hydride abstractions[6] from cyclohexadiene complexes **12** and **13**, we fully anticipated that complex **15** would give **1** ($R = CO_2Me$) upon treatment with triphenylmethyl hexafluorophosphate.

Many attempts in our laboratory to secure the conversion of **15** to **1** ($R = CO_2Me$) failed dismally, the reaction leading to decomposition of the organometallic system. Similar lack of

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