In addition, the ^{13}C NMR chemical shifts of the odd carbons are affected by close dipoles and downfield shifted by polar solvents. C_{13} is a very sensitive carbon (to dipoles and charge delocalization), and its ^{13}C chemical shift in bovine rhodopsin (168.9 ppm)[18] is closely mimicked in model compounds[17] adopting positive-negative charge separation in the Schiff base vicinity (reflected in a red-shifted absorption maximum) and measured in polar solvents (trifluoroethanol). The chemical shifts of other odd-numbered carbons (C_{11}, 141.6; C_9, 148.5; and C_7 132.3)[18] are closely mimicked as well in model compounds, by weakening of the electrostatic interaction in the Schiff base vicinity, however, through introduction of a relatively nonpolar (chloroform) solvent. Thus, it is tempting to suggest that in bovine rhodopsin a weak electrostatic interaction prevails between the positively charged Schiff base linkage and its counterion red shifting the absorption maximum. A relatively polar environment prevails around the C_{13}–N retinal moiety, formed by bound water and/or by protein residues. The negatively charged counterion, which might be close to C_{13}, can be a part of this environment and induces π-electron delocalization due to its large distance from the positively charged Schiff base linkage. A nonpolar environment prevails in the vicinity of the other section of the retinal chromophore (especially around the C_5–C_9 moiety).[7]

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(17) Albeck, A.; Livnah, N.; Gottlieb, H.; Sheves, M. *J. Am. Chem. Soc.* **1992**, *114*, 2400.

(18) Smith, S.; Palings, I.; Miley, M.; Courtin, J.; de Groot, H.; Lugtenburg, J.; Mathies, R.; Griffin, R. *Biochemistry* **1990**, *29*, 8158.

A Mechanistic Study of the Oxidative Addition of H_2 to $W(PMe_3)_4I_2$: Observation of an Inverse Equilibrium Isotope Effect

Daniel Rabinovich and Gerard Parkin*

Department of Chemistry
Columbia University
New York, New York 10027

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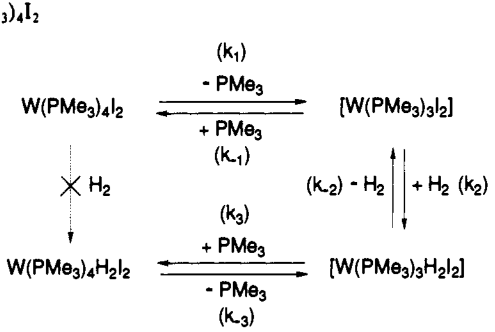
Oxidative addition and its reverse, reductive elimination, are two of the most elementary transformations in organometallic chemistry.[1] In particular, the oxidative addition of dihydrogen represents an important step in many catalytic hydrogenation and hydroformylation processes,[2] and a knowledge of the factors that influence metal-hydrogen bond dissociation energies (BDEs) would provide key information central to understanding, and predicting, reactivity pathways.[3,4] Unfortunately, relatively few metal-hydrogen BDEs have been reported in the literature, in part due to the difficulty of such measurements. Here we report kinetic and thermodynamic studies of the reversible oxidative addition of dihydrogen to six-coordinate *trans*-$W(PMe_3)_4I_2$, which have allowed both (i) the determination of the W-H BDE in $W(PMe_3)_4H_2I_2$ and (ii) the elucidation of the mechanism of the oxidative addition/reductive elimination transformation.

Scheme I. Proposed Mechanism for Oxidative Addition of H_2 to $W(PMe_3)_4I_2$



Sattelberger was the first to report the oxidative addition of H_2 to six-coordinate complexes of the type $M(PR_3)_4Cl_2$ (M = Nb, Ta).[5] Sharp subsequently extended this method for the synthesis of the tungsten analogue $W(PMe_3)_4H_2Cl_2$.[6] Although $W(PMe_3)_4H_2Cl_2$ has been reported to be thermally stable to reductive elimination of dihydrogen,[6] we have found that the iodide analogue $W(PMe_3)_4H_2I_2$[7] undergoes facile reductive elimination of H_2 at 60 °C to give *trans*-$W(PMe_3)_4I_2$.[8] The molecular structures of both six- and eight-coordinate iodide complexes *trans*-$W(PMe_3)_4I_2$ and $W(PMe_3)_4H_2I_2$ have been determined by X-ray diffraction.[9]

Significantly, under 1 atm of H_2, *trans*-$W(PMe_3)_4I_2$ and $W(PMe_3)_4H_2I_2$ exist in equilibrium (eq 1) with comparable concentrations so that the equilibrium constant (K) can readily be measured by using ^1H NMR spectroscopy. The temperature

$$W(PMe_3)_4I_2 + H_2 \overset{K}{\rightleftharpoons} W(PMe_3)_4H_2I_2 \qquad (1)$$

dependence of the equilibrium constant has established the values of $\Delta H° = -19.7$ (6) kcal mol^{-1} and $\Delta S° = -45$ (2) eu for the oxidative addition reaction. Since we may define $\Delta H° = D(\text{H–H}) - 2D(\text{W–H})$ for this reaction,[10] a value of 62.0 (6) kcal mol^{-1} is obtained for the average W-H BDE in $W(PMe_3)_4H_2I_2$.[11] W-H BDEs have previously been reported for only a few complexes, for which a range of 64-73 kcal mol^{-1} has been observed.[12]

Investigation of the corresponding oxidative addition of D_2 to *trans*-$W(PMe_3)_4I_2$ reveals a substantial *inverse* equilibrium deuterium isotope effect, with $K_H/K_D = 0.63$ (5) at 60 °C. The

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1982**, *47*, 205-238. (c) Hay, P. J. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 127-147.

(2) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992. (b) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, Chapter 51, pp 285-363. (c) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.

(3) (a) *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990. (b) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629-688. (c) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55-66.

(4) (a) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79-88. (b) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71-110. (c) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, Chapter 2, pp 43-90. (d) Labinger, J. A.; Bercaw, J. E. *Organometallics* **1988**, *7*, 926-928.

(5) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718-1726.

(6) Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808-1813.

(7) $W(PMe_3)_4H_2I_2$ is readily prepared from $W(PMe_3)_4H_2Cl_2$ by metathesis with excess NaI in benzene solution.

(8) $W(PMe_3)_4I_2$ has also been reported to exist as a diamagnetic cis isomer, but we have not been able to reproduce this result. See: Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204-1211.

(9) *trans*-$W(PMe_3)_4I_2$ is tetragonal, $I\bar{4}2m$ (No. 121), $a = b = 9.742$ (1) Å, $c = 12.424$ (3) Å, $V = 1179.1$ (9) Å^3, $Z = 2$. $W(PMe_3)_4H_2I_2$ is monoclinic, $P2_1$ (No. 4), $a = 9.041$ (3) Å, $b = 14.930$ (8) Å, $c = 9.764$ (4) Å, $V = 1194.7$ (8) Å^3, $Z = 2$.

(10) For a lucid argument that rationalizes this expression, see ref 34 in the following: Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875-1887.

(11) On the basis that $D(\text{H–H}) = 104.2$ kcal mol^{-1} and $D(\text{D–D}) = 106.0$ kcal mol^{-1}. *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1989-1990; p F-199.

(12) $[W(CO)_6H]^+$ (64 (3) kcal mol^{-1}),[12a] (η^5-C_5H_5)$W(CO)_3H$ (73 kcal mol^{-1}),[12b-d] (η^5-C_5H_5)$W(CO)_2(PMe_3)H$ (70 kcal mol^{-1}),[12b,c] (η^5-C_5H_5)$_2WH_2$ (73 (1) kcal mol^{-1}),[12e,f] and (η^5-C_5H_5)$_2W(H)I$ (65 (3) kcal mol^{-1}).[12e,f] (a) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 190-192. (b) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711-6717. Note that the bond dissociation energies listed in Table II of this reference are 8 kcal mol^{-1} lower than the correct values. See the correction (ref 12c). (c) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843. (d) A higher value of 80.7 kcal mol^{-1} has previously been reported for (η^5-C_5H_5)$W(CO)_3H$. See: Landrum, J. T.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 215-224. (e) Calhorda, M. J.; Dias, A. R.; Minas da Piedade, M. E.; Salema, M. S.; Martinho Simões, J. A. *Organometallics* **1987**, *6*, 734-738. (f) Calado, J. C. G.; Dias, A. R.; Martinho Simões, J. A.; Ribeiro da Silva, M. A. V. *J. Organomet. Chem.* **1979**, *174*, 77-80.

0002-7863/93/1515-353$04.00/0

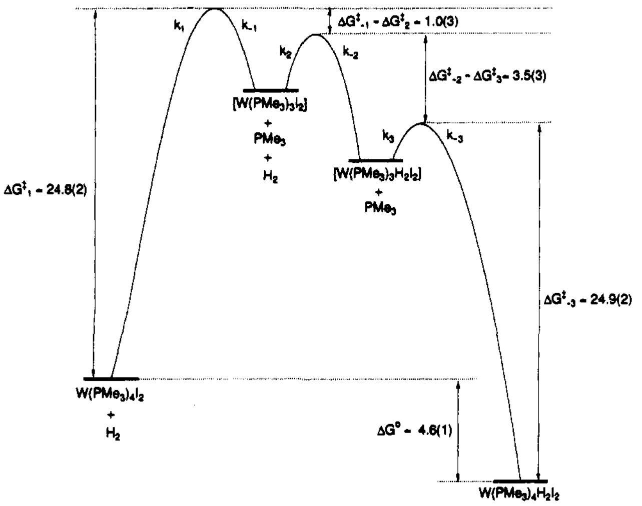

Figure 1. Energy surface for oxidative addition of H_2 to $W(PMe_3)_4I_2$ at 60 °C. Standard states of the components are 1 M, and energy values are in kilocalories/mole.

temperature dependence of K_D reveals that the origin of the inverse equilibrium deuterium isotope effect is enthalpic in nature [$\Delta H°_D = -21.6$ (7) kcal mol^{-1}, compared to $\Delta H°_H = -19.7$ (6) kcal mol^{-1}], since the W–D bond is substantially stronger than the W–H bond [D(W–D) = 63.8 (7) kcal mol^{-1} versus D(W–H) = 62.0 (6) kcal mol^{-1}].[11] Indeed, the small entropic difference [$\Delta S°_D = -51$ (3) eu versus $\Delta S°_H = -45$ (2) eu] actually attempts to counter the inverse nature of the equilibrium deuterium isotope effect.[13]

It is important to emphasize that an inverse equilibrium deuterium isotope effect for oxidative addition would *not* be predicted by consideration of the zero point energy differences associated with the observed W–H and W–D stretching frequencies alone.[14] Therefore, the inclusion of *bending* modes associated with the dihydride moiety is proposed to be responsible for an additional lowering of zero point energy for $W(PMe_3)_4D_2I_2$ with respect to $W(PMe_3)_4H_2I_2$.[15]

The mechanism of the oxidative addition/reductive elimination transformation has been investigated by kinetic studies. Interestingly, $W(PMe_3)_4H_2I_2$ is *not* obtained by the *direct* oxidative addition of H_2 to six-coordinate *trans*-$W(PMe_3)_4I_2$. Specifically, the oxidative addition is strongly inhibited by addition of PMe_3, so that a mechanism involving PMe_3 dissociation and a five-coordinate $[W(PMe_3)_3I_2]$ intermediate is implied. Oxidative addition of H_2 to $[W(PMe_3)_3I_2]$, followed by coordination of PMe_3, gives $W(PMe_3)_4H_2I_2$, as summarized in Scheme I. A similar scheme has previously been proposed by Halpern for hydrogenation of $Rh(PPh_3)_3Cl$.[16] As indicated by microscopic reversibility, the reductive elimination of H_2 from $W(PMe_3)_4H_2I_2$ must also proceed via initial PMe_3 dissociation. Accordingly, the reductive elimination of H_2 from $W(PMe_3)_4H_2I_2$ is also inhibited by addition of PMe_3. A detailed study of the kinetics of the oxidative addition and reductive elimination transformations has allowed the free-energy surface illustrated in Figure 1 to be established.[17] The primary kinetic deuterium isotope effect for oxidative addition of H_2 is $k_{2(H)}/k_{2(D)} = 1.2$ (2)],[18] whereas that for reductive elimination of H_2 is estimated to be $k_{-2(H)}/k_{-2(D)} \approx 2$.[19] Hence, since the kinetic deuterium isotope effect for reductive elimination is substantially larger than that for oxidative addition, an inverse equilibrium deuterium isotope effect is obtained.[20,21]

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Supplementary Material Available: Kinetic and thermodynamic data for the $W(PMe_3)_4I_2/H_2(D_2)$ systems and crystal structure data for $W(PMe_3)_4I_2$ and $W(PMe_3)_4H_2I_2$ (17 pages); listing of observed and calculated structure factors for $W(PMe_3)_4I_2$ and $W(PMe_3)_4H_2I_2$ (20 pages). Ordering information is given on any current masthead page.

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[13] The origin of the difference in $\Delta S°$ for the oxidative addition of H_2 and D_2 is presumably the greater entropy of D_2 compared with that of H_2 (39.0 and 34.0 eu, respectively, at 300 K). See: Woolley, H. W.; Scott, R. B.; Brickwedde, F. G. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1948**, *41*, 379–475.

[14] The observed ν_{W-H} and ν_{W-D} stretching frequencies of 1961 and 1416 cm^{-1}, respectively, result in a zero point energy difference of 273 cm^{-1} for this vibrational mode. If the symmetric and asymmetric stretches have similar frequencies, the combined zero point energy lowering would be less than the difference between D_2 and H_2 zero point energies (630 cm^{-1}), so that consideration of additional vibrational modes is required to produce the inverse equilibrium deuterium isotope effect.

[15] Relatively little information is available concerning the bending modes associated with transition metal hydride complexes. For a recent study on $[(\eta^5\text{-}C_5H_5)_2MH_n]^{x+}$ complexes, see: Girling, R. B.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1986**, *25*, 31–36.

[16] (a) Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629–630. (b) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65–68. (c) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11–19.

[17] It is likely that a dihydrogen species, for example, $[W(PMe_3)_3(\eta^2\text{-}H_2)I_2]$, may also be an intermediate on the energy surface. However, since our data is not capable of providing support either for or against such intermediates, we have excluded them from our treatment.

[18] The kinetic deuterium isotope effect for addition of H_2 to *trans*-$Ir(PPh_3)_2(CO)Cl$ is of a similar magnitude ($k_H/k_D = 1.06$ at 30 °C). Zhou, P.; Vitale, A. A.; San Filippo, J., Jr.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 8049–8054.

[19] The estimate $k_{-2(H)}/k_{-2(D)} \approx 2$ is based on the assumption that the secondary isotope effect for addition of PMe_3 to $[W(PMe_3)_3H_2I_2]$ is negligible (i.e., $k_{3(H)}/k_{3(D)} \approx 1$).

[20] An inverse equilibrium deuterium isotope effect has also been observed for the oxidative addition of dihydrogen to *trans*-$Ir(PPh_3)_2(CO)Cl$.[20a-c] A composite primary and secondary inverse equilibrium deuterium isotope effect has also been observed for the oxidative addition of dihydrogen to $Cp_2Ta(\mu\text{-}CX_2)_2Ir(CO)(PPh_3)$ (X = H, D).[20d] (a) Vaska, L.; Werneke, M. F. Manuscript in preparation. (b) Werneke, M. F. Ph.D. Thesis, Clarkson College of Technology, Potsdam, NY, 1971. (c) Goldman, A. Personal communication. (d) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 7629–7636.

[21] For a review of isotope effects in reactions of transition metal hydrides, see: Bullock, R. M. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 263–307.

Generation of Enantiopure *trans*-$\Delta^{9,10}$-Tricyclo[9.3.1.$0^{3,8}$]pentadecene Diastereomers from a Single Precursor. Control of Stereochemistry by Means of Rotationally Restrictive Nonbonded Interactions

Leo A. Paquette* and Mangzhu Zhao

Evans Chemical Laboratories
The Ohio State University
Columbus, Ohio 43210

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The resolvability and optical stability of medium-sized *trans*-cycloalkenes has been of interest for 30 years.[1-3] Molecular asymmetry of this type can be established because of steric inhibition to internal rotation relative to the remainder of the ring of the σ-bonds flanking the (*E*)-alkene subunit. Although the structural implications of these factors are well understood, they have to our knowledge never been applied in a synthetic context. Our interest in the de novo acquisition of taxanes[4] has led us to

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[1] (a) Cope, A. C.; Ganellin, C. R.; Johnson, H. W., Jr.; Van Auken, T. V.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1963**, *85*, 3276. (b) Cope, A. C.; Mehta, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 1268. (c) Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc.* **1965**, *87*, 3649.

[2] Cope, A. C.; Hecht, J. K.; Johnson, H. W., Jr.; Keller, H.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1966**, *88*, 761.

[3] Cope, A. C.; Banholzer, K.; Keller, H.; Pawson, B. A.; Whang, J. J.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3644.