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Deuterium and Tritium Equilibrium Isotope Effects for Coordination and Oxidative Addition of Dihydrogen to [W(CO)$_5$] and for the Interconversion of W(CO)$_5$(η^2-H$_2$) and W(CO)$_5$H$_2$

Kevin E. Janak and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027

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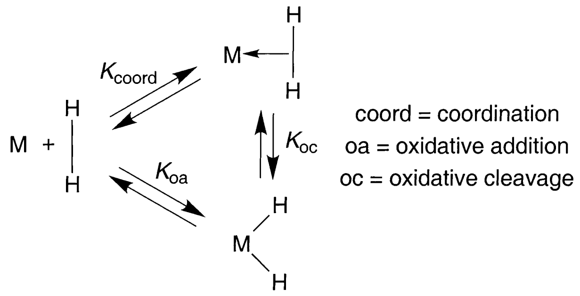
Summary: DFT (B3LYP) calculations demonstrate that the equilibrium isotope effects (EIEs) for coordination and oxidative addition of H_2 to [W(CO)$_5$] do not exhibit a simple exponential variation with temperature; rather, the EIEs exhibit a maximum, with the EIEs being inverse (<1) at low temperature and normal (>1) at high temperature. At each temperature, the EIE for coordination of dihydrogen is less than that for oxidative addition, such that the EIE for the interconversion of W(CO)$_5$(η^2-H$_2$) is normal, with deuterium favoring the nonclassical (dihydrogen) site at all temperatures.

One of the most fundamental concepts in organometallic chemistry is that the interaction between a transition metal and dihydrogen may be represented by a continuum of structures, with extremes that are represented as dihydrogen [M(η^2-H$_2$)] and dihydride [MH$_2$] complexes (Scheme 1).[1] Regardless of the precise nature of the interaction between the metal center and dihydrogen, the equilibrium isotope effects (EIEs) that have been reported for binding H_2 are almost invariably *inverse*, i.e. $K_H/K_D < 1$, such that D_2 interacts more favorably than H_2.[2−5] However, we have recently reported that the situation is more complex than originally appreciated.[6] In this paper, we pursue further details of the interaction of dihydrogen with a metal center by determining the temperature dependence of the EIEs for (i) the coordination of dihydrogen and (ii) the interconversion of dihydrogen and dihydride complexes.

Scheme 1



Closely following the synthesis of the first dihydrogen complexes, M(CO)$_3$(PR$_3$)$_2$(η^2-H$_2$) (M = Mo, W; R = Pr^i, Cy),[7] the pentacarbonyl counterparts M(CO)$_5$(η^2-H$_2$) (M = Cr, Mo, W) were generated and spectroscopically characterized at low temperature in both liquid xenon solution[8] and argon matrices.[9,10] In view of their simplicity, M(CO)$_5$(η^2-H$_2$) and M(CO)$_5$H$_2$ derivatives are particularly attractive for computational studies[11] to evaluate the EIEs pertaining to the interactions of dihydrogen with a transition-metal center. Therefore, we have performed DFT (B3LYP) calculations[12] on the tungsten complexes W(CO)$_5$(η^2-H$_2$) and W(CO)$_5$H$_2$ to determine the EIEs for (i) coordination of H_2, (ii) oxidative addition of H_2, and (iii) interconversion of W(CO)$_5$(η^2-H$_2$) and W(CO)$_5$H$_2$.

Equilibrium isotope effects are typically computed by using the expression EIE = K_H/K_D = SYM·MMI·EXC·

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[1] (1) (a) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory, and Reactivity*; Kluwer Academic/Plenum Publishers: New York, 2001. (b) Kubas, G. J. *J. Organomet. Chem.* **2001**, *635*, 37−68.

[2] (2) (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353−354. (b) Hascall, T.; Rabinovich, D.; Murphy, V. J.; Beachy, M. D.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 11402−11417.

[3] (3) (a) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019−8023. (b) Shin, J. H.; Parkin, G. *J. Am. Chem. Soc.* **2002**, *124*, 7652−7653. (c) Yan, S. G.; Brunschwig, B. S.; Creutz, C.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1998**, *120*, 10553−10554.

[4] (4) (a) Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179−9190. (b) Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *177*, 115−120. (c) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208−214. (d) Bakhmutov, V. I.; Bertrán, J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Modrego, J.; Oro, L. A.; Sola, E. *Chem. Eur. J.* **1996**, *2*, 815−825.

[5] (5) Bullock, R. M.; Bender, B. R. Isotope Methods in Homogeneous Catalysis. In *Encyclopedia of Catalysis*; Horváth, I. T., Ed.; 2002.

[6] (6) (a) Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 6889−6891. (b) Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.*, in press.

[7] (7) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451−452.

[8] (8) (a) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27−30. (b) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645−3651. (c) Andreá, R. R.; Vuurman, M. A.; Stufkens, D. J.; Oskam, A. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 372−374.

[9] (9) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374−2379.

[10] (10) M(CO)$_5$(η^2-H$_2$) has also been studied in cyclohexane solution at room temperature[10a] and in the gas phase.[10b−d] (a) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30−32, observed in the gas phase using time-resolved IR spectroscopy. See: (b) Ishikawa, Y.; Weersink, R. A.; Hackett, P. A.; Rayner, D. M. *Chem. Phys. Lett.* **1987**, *142*, 271−274. (c) Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Phys. Chem.* **1989**, *93*, 652−657. (d) Wells, J. R.; House, P. G.; Weitz, E. *J. Phys. Chem.* **1994**, *98*, 8343−8351.

[11] (11) For other computational studies on M(CO)$_5$(η^2-H$_2$), see: (a) Li, J.; Ziegler, T. *Organometallics* **1996**, *15*, 3844−3849. (b) Tomàs, J.; Lledós, A.; Jean, Y. *Organometallics* **1998**, *17*, 4932−4939. (c) Nemcsok, D. S.; Kovács, A.; Rayón, V. M.; Frenking, G. *Organometallics* **2002**, *21*, 5803−5809. (d) Dapprich, S.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 354−357. (e) Dapprich, S.; Frenking, G. *Organometallics* **1996**, *15*, 4547−4551.

[12] (12) All calculations were carried out using DFT as implemented in the Jaguar 4.1 suite of ab initio quantum chemistry programs. See the Supporting Information for details.

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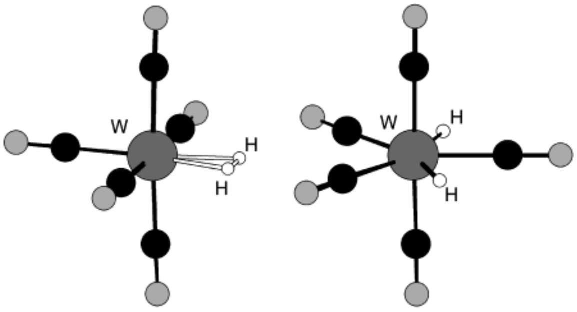

Figure 1. Geometry-optimized structures of $W(CO)_5(\eta^2\text{-}H_2)$ and $W(CO)_5H_2$.

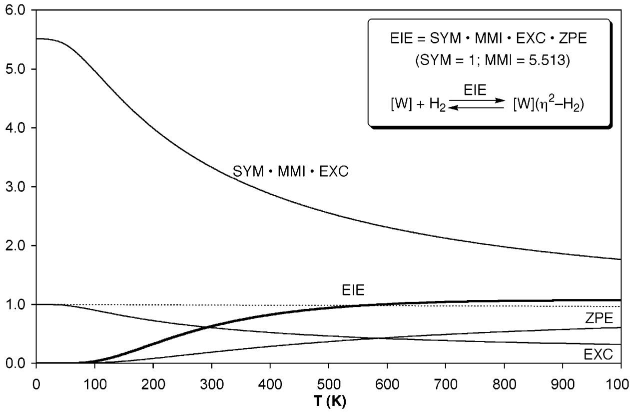

Figure 2. Calculated EIE as a function of temperature for coordination of H_2 and D_2 to $[W(CO)_5]$.

ZPE, where SYM is the symmetry factor, MMI is the mass-moment of inertia term, EXC is the excitation term, and ZPE is the zero point energy term.[13,14] Application of this expression requires knowledge of both the structures and vibrational frequencies of the reactant molecules. The geometry-optimized structures of $W(CO)_5(\eta^2\text{-}H_2)$ and $W(CO)_5H_2$ are illustrated in Figure 1.[15,16]

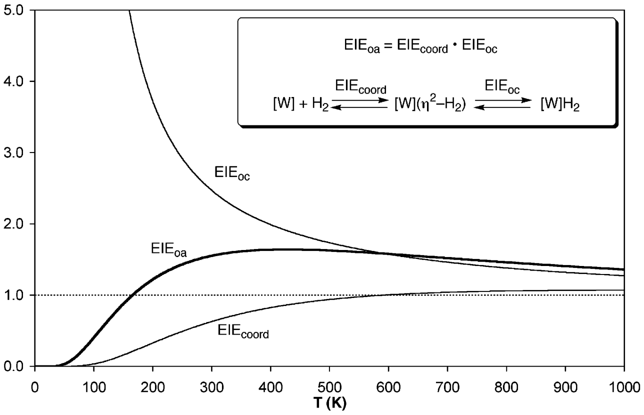

Figure 3. Calculated EIE as a function of temperature for oxidative addition of H_2 and D_2 to $[W(CO)_5]$ and for oxidative cleavage of $W(CO)_5(\eta^2\text{-}H_2)$ to $W(CO)_5H_2$.

The temperature dependence of the EIE for coordination of H_2 to form the dihydrogen complex $W(CO)_5(\eta^2\text{-}H_2)$ is illustrated in Figure 2. In accord with the experimental reports of inverse EIEs for coordination of H_2 in other systems, the EIE for coordination of H_2 to $[W(CO)_5]$ is likewise calculated to be inverse at ambient temperature.[17] However, at high temperature, the EIE is calculated to become normal.[18] The temperature dependence of the EIE for oxidative addition of H_2 exhibits a profile similar to that for coordination of H_2 (Figure 3), with the notable difference that the transition from an inverse to a normal EIE occurs at a much lower temperature (170 K) than that for coordination (580 K).[19] As illustrated for coordination of H_2 in Figure 2, the existence of maxima in the temperature dependencies of the EIEs for the interaction of H_2 is a result of the temperature dependencies of the ZPE and EXC terms opposing each other since the SYM and MMI terms are temperature independent.[20] Furthermore, examination of the temperature dependencies of the ZPE (enthalpy) and combined [SYM·MMI·EXC] (entropy) terms demonstrates that it is the ZPE term which causes the EIE to be inverse at low temperature. The inverse ZPE term is a consequence of the fact that association with H_2 (be it forming either a dihydrogen or a dihydride complex) creates *five* new isotopically sensitive vibrations (derived from the rotational and translational degrees of freedom of the H_2 molecule) of sufficient energy that isotopic substitution results in a greater ZPE change for the adduct than for H_2.[2−4a]

Although $W(CO)_5(\eta^2\text{-}H_2)$ has been studied by IR spectroscopy,[8] the complete set of isotope-sensitive vibrational frequencies are not known. Experimental vibrational data are, nevertheless, available for both $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ and $W(CO)_3(PCy_3)_2(\eta^2\text{-}D_2)$,[4a] which thereby allows for the temperature dependence of the EIE for coordination of H_2 and D_2 to $[W(CO)_3(PCy_3)_2]$ to be predicted. Thus, employing the experimentally determined vibrational frequencies for $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ and $W(CO)_3(PCy_3)_2(\eta^2\text{-}D_2)$, the EIE is predicted to pass from an inverse value[21] at ambient temperature

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[13] (a) Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 225−242. (b) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980. (c) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley-Interscience: New York, 1984.

[14] For seminal studies concerned with the computation of isotope effects in organometallic systems, see: (a) Slaughter, L. M.; Wolczanski, P. T.; Klinckman, T. R.; Cundari, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7953−7975. (b) Bender, B. R. *J. Am. Chem. Soc.* **1995**, *117*, 11239−11246. (c) References 3a and 4a.

[15] The derived structure is similar to the results of previous calculations on $(CO)_5W(\eta^2\text{-}H_2)$.[11]

[16] Pentagonal-bipyramidal $W(CO)_5H_2$ is 15.6 kcal mol^{-1} higher in energy than $(CO)_5W(\eta^2\text{-}H_2)$ (DFT B3LYP with cc-pVTZ(-f)/LACV3P** basis sets). $W(CO)_5H_2$ with *cis*-dihydride ligands and a $[W(CO)_5]$ geometry similar to that of $W(CO)_5(\eta^2\text{-}H_2)$ is not a stable stationary point and converges to the dihydrogen complex during geometry optimization.[11b]

[17] Although the EIE itself has not been reported, an inverse EIE (0.38) is suggested from the rate constants for (i) coordination of H_2/D_2 to $Cr(CO)_5(C_6H_{12})$ ($k_H/k_D = 19\,000/10\,000 = 1.9$) and (ii) dissociation of hydrogen from $Cr(CO)_5(\eta^2\text{-}H_2)$ ($k_H/k_D = 2.5/0.5 = 5.0$), assuming that the cyclohexane does not play a significant role.[10a]

[18] A normal EIE has also been calculated for coordination of H_2 and D_2 to $[CpRu(H_2PCH_2PH_2)]^+$ and $[Os(H_2PCH_2CH_2PH_2)]^+$ at 300 K; however, the temperature dependence and the notion of a maximum for the EIE was not discussed (Torres, L.; Gelabert, R.; Moreno, M.; Lluch, J. M. *J. Phys. Chem. A* **2000**, *104*, 7898−7905). On the basis of the reported ZPE terms (0.323 and 0.505, respectively), we predict that these EIEs will also become inverse at low temperature.

[19] For other examples involving H_2 for which both normal and inverse EIEs have been discussed, see: Kotaka, M.; Okamoto, M.; Bigeleisen, J. *J. Am. Chem. Soc.* **1992**, *114*, 6436−6445.

[20] The combined [SYM·MMI] term is equivalent to the product of the translational and rotational partition function ratios of the products and reactants, i.e. $(Q_{tr}^{P})(Q_{rot}^{P})/(Q_{tr}^{R})(Q_{rot}^{R})$. This term is only strictly temperature independent when $T \gg \Theta_{rot}$, the rotational temperature. However, this variation has no effect on the actual low-temperature limit of the EIE.

[21] Experimental EIE = 0.70 at 22 °C.[4a]

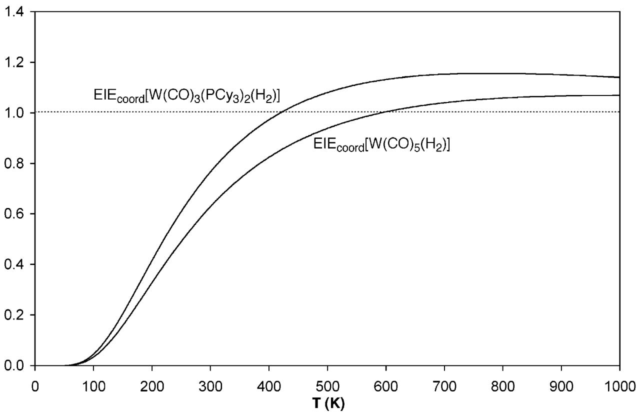

Figure 4. Comparison of the calculated EIE for coordination of H_2 and D_2 to $[W(CO)_5]$ using computed frequencies with that for $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ using experimentally determined frequencies.

to a normal value at high temperature, before returning to unity at infinite temperature (Figure 4). The similarity of the temperature dependence of the EIE for coordination of H_2/D_2 to $[W(CO)_5]$ using *calculated* frequencies to that for $[W(CO)_3(PCy_3)_2]$ using *experimental* frequencies is significant, since it provides support for the use of calculated frequencies in predicting isotope effects and also suggests that the inverse–normal transition may be general for dihydrogen complexes.[22]

Another important aspect concerned with the EIEs for formation of $W(CO)_5(\eta^2\text{-}H_2)$ and $W(CO)_5H_2$ pertains to whether deuterium prefers to be located in the classical (dihydride) site or nonclassical (dihydrogen) site. This issue is of some interest because of contradictory reports in the literature. For example, (i) experimental studies on $CpNb(CO)_3(\eta^2\text{-}H_2)/CpNb(CO)_3H_2$[23] and $[Re(PR_3)_3(CO)(\eta^2\text{-}H_2)H_2]^+/[Re(PR_3)_3(CO)H_4]^+$ ($PR_3 = PMe_2Ph$,[24] PMe_3[25]) and calculations on $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)/W(CO)_3(PH_3)_2H_2$[26] indicate that deuterium favors the nonclassical site, while (ii) experimental studies on $[TpIr(PMe_3)(\eta^2\text{-}H_2)H]^+$[27] and $[Cp_2W(\eta^2\text{-}H_2)H]^+$[28] indicate that deuterium favors the classical site. In this regard, the EIE for conversion of $W(CO)_5(\eta^2\text{-}H_2)$ to $W(CO)_5H_2$ is calculated to be normal at all temperatures, thereby demonstrating that deuterium favors the nonclassical site in this system (Figure 3).[29]

While it is evident that the normal EIE_{oc} for conversion of $W(CO)_5(\eta^2\text{-}H_2)$ to $W(CO)_5H_2$ is a direct result of the fact that $EIE_{oa} > EIE_{coord}$ (since $EIE_{oc} = EIE_{oa}/EIE_{coord}$), more detailed examination indicates that the EIE is dominated by the ZPE term. Thus, since $W(CO)_5(\eta^2\text{-}H_2)$ and $W(CO)_5H_2$ have the same number of isotopically sensitive vibrations, the normal ZPE term results purely from the fact that the ZPE associated with the H–H fragment in $W(CO)_5(\eta^2\text{-}H_2)$ is greater than that of the two W–H bonds in $W(CO)_5H_2$. Indeed, a normal ZPE term would be predicted for this transformation merely on the basis of the simple notion that deuterium prefers to be located in the stronger bond, i.e. D–D versus M–D.[30] While there is a total of six isotopically sensitive normal modes associated with a $[MH_2]$ moiety, the single most important mode is that which corresponds to the high-energy H–H stretch in $W(CO)_5(\eta^2\text{-}H_2)$ (ν_{H-H} 3330 cm^{-1}; ν_{D-D} 2366 cm^{-1}) and which becomes a low-energy symmetric bend in $W(CO)_5H_2$ (ν_{HMH} 784 cm^{-1}; ν_{DMD} 600 cm^{-1}): the ZPE differences for these vibrations clearly favor deuterium residing in the nonclassical site.

In addition to the use of deuterium, tritium has also found applications in the NMR spectroscopic characterization of dihydrogen and hydride complexes.[31] Therefore, we have calculated the corresponding EIEs for tritium: i.e., K_H/K_T. For the interconversion of $W(CO)_5(\eta^2\text{-}H_2)$ and $W(CO)_5H_2$, K_H/K_T is greater than K_H/K_D at all temperatures, such that tritium favors the nonclassical site. This preference is in accord with the aforementioned fact that the EIE is dominated by the ZPE term. In contrast to the simple $K_H/K_T > K_H/K_D$ relationship for interconversion of $W(CO)_5(\eta^2\text{-}H_2)$ and $W(CO)_5H_2$, coordination and oxidative addition of dihydrogen are both characterized by regions in which $K_H/K_T > K_H/K_D$ *and* in which $K_H/K_T < K_H/K_D$. Specifically, $K_H/K_T < K_H/K_D$ at low temperature when the EIE is dominated by the ZPE (enthalpy) term, and $K_H/K_T > K_H/K_D$ at high temperature when the EIE is dominated by the [SYM·MMI·EXC] (entropy) term. A corollary of these observations is that the temperature dependence of K_D/K_T for both coordination and oxidative addition of dihydrogen exhibits inverse and normal regions, analogous to that described above for K_H/K_D.

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Supporting Information Available: Text and tables giving computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Although the qualitative forms of the EIEs for coordination of H_2 to $[W(CO)_3(PCy_3)_2]$ and $[W(CO)_5]$ are similar, there is a quantitative difference since the systems have different ligands. Furthermore, consideration of anharmonicity will also lower the temperature at which the computed EIE undergoes a transition from inverse to normal, because the ZPE term is more strongly influenced than the EXC term. See: Torres, L.; Gelabert, R.; Moreno, M.; lluch, J. M. *J. Phys. Chem. A* **2000**, *104*, 7898.

(23) Haward, M. T.; George, M. W.; Hamley, P.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1101–1103.

(24) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912–6918.

(25) Gusev, D. G.; Nietlispach, D.; Eremenko, I. L.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3628–3636.

(26) Torres, L.; Moreno, M.; Lluch, J. M. *J. Phys. Chem. A* **2001**, *105*, 4676–4681.

(27) (a) Heinekey, D. M.; Oldham, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 3137–3138. (b) Oldham, W. J.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028–11036.

(28) Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Dalton Trans.* **1993**, 3431–3439.

(29) The EIEs calculated here assume the harmonic oscillator approximation for the individual bonds. More complete analyses would include effects due to anharmonicity. However, calculations on the conversion of $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ to $W(CO)_3(PH_3)_2H_2$ indicate that the influence of anharmonicity on the EIE at 300 K is relatively small ($EIE_{harm} = 2.06$ and $EIE_{anharm} = 1.87$).[30]

(30) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225–233.

(31) See, for example: Law, J. K.; Mellows, H.; Heinekey, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 1024–1030.