Theoretical Study of Primary and Secondary Deuterium Equilibrium Isotope Effects for H_2 and CH_4 Addition to *trans*-Ir$(PR_3)_2$(CO)X

Faraj Abu-Hasanayn, Karsten Krogh-Jespersen,* and Alan S. Goldman*

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

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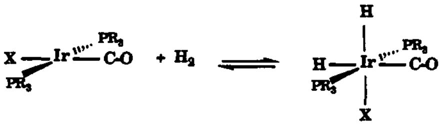
Abstract: Deuterium equilibrium isotope effects (EIE) for H_2 and H–CH_3 addition to Vaska-type complexes, *trans*-Ir$(PH_3)_2$(CO)X (XM), have been determined using vibrational frequencies obtained from ab initio calculations on XM and on *cis,trans*-H_2Ir$(PH_3)_2$(CO)X (XMH_2). Inverse primary EIE values for H_2/D_2 addition to XM are computed to be 0.46 (X = Cl), 0.57 (X = CH_3), and 0.33 (X = H; 0.66 after statistical normalization) at 300 K. The EIE values and the computed enthalpy and entropy terms are consistent with several experimental studies. Secondary thermodynamic deuterium isotope effects for H_2 addition to XM are computed for X = H/D (α-EIE = 0.44; 0.88 after statistical normalization) and for X = CH_3/CD_3 (β-EIE = 0.86). Computations on the addition of CH_4/CH_3D or CH_4/CD_4 to HM reveal EIEs of 7.77 (1.94 per bond) and 3.64, respectively. These results are analyzed and discussed using equilibrium statistical mechanics.

Introduction

Since the discovery of Vaska's complex (*trans*-Ir$(PPh_3)_2$(CO)-Cl) 30 years ago, the reversible oxidative addition of H_2 (eq 1) has been considered one of the most interesting and characteristic reactions of transition-metal chemistry.[1,2] It is now a fundamental elementary step in numerous catalytic systems.[3] In the past decade, a closely related reaction, oxidative addition of C–H bonds (particularly those of alkanes),[4] has also been the focus of great interest, largely in the context of incorporating it into catalytic cycles as well.[5] Both reactions have been the subject of extensive and revealing computational studies.[6]

The measurement of isotope effects[7] is an important tool in the mechanistic study of stoichiometric and catalytic reactions involving the addition of H_2 and C–H bonds.[8] Several studies have relied on computed frequencies to calculate isotope effects in organic reaction systems.[9] Morokuma *et al.*[10] have used computed frequencies to study the deuterium kinetic isotope effects for H_2 and CH_4 addition to Pt$(PH_3)_2$. As part of our ongoing ab initio computational study of addition to d^8 square-planar complexes,[11] we have examined H/D kinetic isotope effects (KIE) relevant to eq 1.[12] The experimental KIE value k_H/k_D for eq 1 (X = Cl; R = Ph) has been experimentally determined with good precision.[13-15] Our calculation (R = H) is in excellent agreement with the experimental value and has elucidated the several factors from which the final KIE is composed.[12]

$$trans\text{-}Ir(PR_3)_2(CO)X + H_2 \rightleftharpoons cis,trans\text{-}H_2Ir(PR_3)_2(CO)X \quad (1)$$



The equilibrium isotope effect (EIE) for eq 1 and related reactions has been examined much less extensively. The EIE is critical when interpreting results of isotope-labeling studies on multistep stoichiometric or catalytic systems in which H_2 or C–H addition is a preequilibrium step. Measured "kinetic" isotope effects for such reactions often simply reflect EIEs of steps prior

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to the rate-determining step. Further, the ability to predict an EIE, in combination with the KIE for either oxidative addition or reductive elimination, reveals the KIE for the respective reverse reaction.

Our calculations in this study predict a significantly "inverse" EIE ($K_{H_2}/K_{D_2} < 1$) for eq 1 (ca. 0.5) which we have confirmed experimentally. On the basis of factors related to vibrational frequencies alone, an even stronger inverse EIE would be predicted for eq 1 (ca. 0.1), but a normal mass moment of inertia term (5.66) partially cancels this out to give the actual value.

Our conclusions about the EIEs (unlike the KIEs) are expected to be general for the formation of metal hydrides with similar metal–hydrogen vibrational frequencies. Accordingly, Bergman[16] and Parkin[17] have very recently reported similarly inverse EIEs for H_2/D_2 addition to $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)PPh_3$ and $W(PMe_3)_4I_2$, respectively. They also determined the individual entropy and enthalpy terms of the EIE which favor H_2 and D_2 addition, respectively; their findings strongly support our analysis of the individual terms from which the overall EIE value is composed.

In contrast to H_2 addition, the EIEs for $H\text{–}CH_3/D\text{–}CH_3$ and $H\text{–}CH_3/CD_3$ addition to *trans*-$Ir(PH_3)_2(CO)H$ (HM; M = *trans*-$Ir(PH_3)_2CO$) are calculated to be normal. Model complexes with X = H and CH_3 also allow the study of α- and β-secondary isotope effects on H_2 and C–H addition; our results indicate that these EIEs are inverse. Importantly, the computations permit a thorough analysis of the various factors contributing to the EIEs.

Background

To describe how isotopic substitution of a species, A, influences the thermodynamics of its reaction to give B (eq 2), an isotopic exchange equilibrium is written as shown in eq 3 with an asterisk, by convention, denoting the heavier isotopically labeled species.

$$A \rightleftharpoons B \tag{2}$$

$$A + B^* \rightleftharpoons A^* + B \tag{3}$$

The EIE is then defined as the equilibrium constant of eq 3. An EIE value less than unity is inverse, i.e., heavy-isotope labeling of A favors the formation of B in eq 2. When the isotopic substitution is at a bond that is broken or formed in the transformation from A to B, the EIE is said to be primary. A secondary EIE concerns isotope labeling at spectator bonds. Secondary EIEs resulting from substitution at positions one or two bonds removed from a bond that is broken during the reaction are further classified as α- and β-secondary, respectively.

A statistical mechanics[18] treatment of the isotopic equilibrium in eq 3 gives the EIE in terms of the individual partition functions of the reactants and products, as given in eq 4

$$\mathrm{EIE} = \left(\frac{Q_{\mathrm{tr}}^{A^*}Q_{\mathrm{rot}}^{A^*}Q_{\mathrm{vib}}^{A^*}}{Q_{\mathrm{tr}}^{A}Q_{\mathrm{rot}}^{A}Q_{\mathrm{vib}}^{A}}\right)\left(\frac{Q_{\mathrm{tr}}^{B}Q_{\mathrm{rot}}^{B}Q_{\mathrm{vib}}^{B}}{Q_{\mathrm{tr}}^{B^*}Q_{\mathrm{rot}}^{B^*}Q_{\mathrm{vib}}^{B^*}}\right)e^{-(\Delta\Delta\mathrm{ZPE}/RT)} \tag{4}$$

where $Q_{\mathrm{tr}} = (2\pi mkT)^{3/2}/h^3$, $Q_{\mathrm{rot}} = 8\pi^2 IkT/\sigma h^2$ (linear molecules) or $Q_{\mathrm{rot}} = 8\pi^2(8\pi^3 I_A I_B I_C)^{1/2}(kT)^{3/2}/\sigma h^3$ (nonlinear molecules), $Q_{\mathrm{vib}} = \prod_i 1/(1 - e^{-(h\nu_i/kT)})$, $\Delta\Delta\mathrm{ZPE} = \Delta\mathrm{ZPE}_B^{B^*} - \Delta\mathrm{ZPE}_A^{A^*}$, $\Delta\mathrm{ZPE}_A^{A^*} = \mathrm{ZPE}^A - \mathrm{ZPE}^{A^*}$, $\mathrm{ZPE} = \sum_i(h\nu_i/2)$ (zero point energy), m = molecular mass, h = Planck constant, k = Boltzmann constant, T = absolute temperature, R = gas constant, I = moment of inertia, σ = symmetry number, and ν_i = normal mode vibrational frequency with index i covering all normal modes of the molecule.

Alternatively, the EIE can be computed using the simplified treatment of isotope effects developed by Bigeleisen[19] (eq 5) which requires knowledge of only the vibrational frequencies.

$$\mathrm{EIE} = \frac{(\sigma_A^*/\sigma_A)f[A^*/A]}{(\sigma_B^*/\sigma_B)f[B^*/B]} \tag{5}$$

$$f[A^*/A] = \prod \frac{u_i^{A^*}(1 - e^{-u_i^{A}})}{u_i^{A}(1 - e^{-u_i^{A^*}})} e^{(u_i^{A} - u_i^{A^*})/2}, \quad u_i = h\nu_i/kT$$

Generally, in this work, we obtain very similar values using either eq 4 or 5. The full expression (eq 4), however, has the advantage of being more amenable to interpretation. The right side of eq 4 can be conveniently written as a product of four terms EIE = SYM × MMI × EXC × EXP(ZPE) where SYM is the symmetry number ratio factored out of the rotational partition function ratio, MMI is the mass moment of inertia contribution to EIE, EXC is the vibrational excitation component, and EXP(ZPE) is the zero point energy term. The first three terms determine the entropy contribution to EIE while the last term dominates the enthalpy contribution. The SYM and MMI terms can be obtained easily from structural information. The EXC and EXP(ZPE) terms, on the other hand, require a detailed knowledge of the vibrational frequencies of the individual isotopomers for their evaluation; these are the basic entities obtained from the ab initio calculations in this study.

Results and Discussion

Normal Mode Analysis. Vibrational frequencies are obtained from normal mode analysis on the optimized XM and XMH_2 geometries (see Computational Details). Table I contains important computed and experimental frequencies for $ClMH_2$ and *cis,trans*-$H_2Ir(PPh_3)_2(CO)Cl$ (**2**-h_2) and their deuterated analogs ($ClMD_2$ and **2**-d_2). The computed frequencies are about 10% larger than the experimental values, which is a common result in ab initio Hartree–Fock calculations arising primarily because vibronic anharmonicity and electron correlation effects are not included.[20,21] As is commonly practiced,[9,20] this discrepancy can be resolved by scaling of the computed frequencies prior to their use in the EIE calculations. A scaling factor of 0.92 is used herein as it reproduces the exact Ir–H stretching frequencies, X = Cl. Computed scaled frequencies are also used for CH_4. For H_2 and D_2, we used the experimental frequencies (4395 and 3118 cm^{-1}, respectively).[18] Six of the computed normal modes in the dihydride complexes can be assigned as essentially intrinsic Ir–H modes on the basis of vector components, and their frequencies are given in Table I. The two Ir–H stretching modes (formally symmetric and antisymmetric combinations) are only weakly coupled to each other, with the higher stretching frequency corresponding to the hydride trans to Cl (ν_{H1}, 2379 cm^{-1}, unscaled). The weaker stretching mode of the hydride positioned cis to Cl (ν_{H2}, 2283 cm^{-1}) is strongly coupled with the CO stretching mode (ν_{CO}, 2152 cm^{-1}). It is known that as a result of the $\nu_{Ir\text{–}H}/\nu_{CO}$ coupling in **2**-h_2, the formally carbonyl stretching frequency shifts to a higher value upon deuteration (from 1982 cm^{-1} in **2**-h_2 to 2003 cm^{-1} in **2**-d_2).[22] This effect is reproduced very well by the computations since ν_{CO} shifts from 2151 cm^{-1} in $ClMH_2$ to 2176 cm^{-1} in $ClMD_2$, an important result since such vibrational changes taking place upon isotopic labeling enter directly into the EIE calculations. For the out-of-plane bending modes, the computations provide unscaled (scaled) values of 1088 (1001) and 978 (899) cm^{-1} (δ_{out1} and δ_{out2}, Table I) and for the in-plane bending modes values of 1017 (936) and 869 (799) cm^{-1} (δ_{in1} and δ_{in2}, respectively). These values are in reasonably good agreement with the two Ir–H vibrations observed in the IR spectrum of

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Table I. Computed and Experimental M–H, M–D, and CO Vibrational Frequencies for $ClMH_2$ and $ClMD_2$[a]

	computed[b]		experimental[c]	
assignment	$ClMH_2$	$ClMD_2$	**2**-h_2	**2**-d_2
		M–H		
ν_1	2379	1687	2196	1575
ν_2	2283	1600	2100	1497
δ_{out1}	1088	810	843, 829[d]	
δ_{out2}	975	706		
δ_{in1}	1017	737		
δ_{in2}	869	702		
		CO		
ν_{CO}	2151	2176	1982	2003

[a] Values in cm^{-1}. [b] Unscaled values. [c] Reference 22. [d] Values for *cis,trans*-$H_2Ir(AsPh_3)_2(CO)Cl$, ref 15 (unassigned).

$H_2Ir(AsPh_3)_2(CO)Cl$,[15] 843 and 829 cm^{-1}. Each of the calculated bending modes has a dominant contribution from only one hydride, with the larger values corresponding to the hydride trans to Cl. These bending frequencies are of moderate magnitude and prove to be crucial in accurately calculating the isotope effects in this system.

H_2/D_2 Addition to XM (X = Cl, CH_3): Primary Isotope Effects. Application of eq 4 to the equilibrium in eq 6 using computed frequencies for X = Cl and CH_3 gives primary EIEs for H_2/D_2 addition to XM of 0.46 and 0.57, respectively (all EIE values are given for $T = 300$ K, unless noted otherwise; Table II). Changing

$$H_2 + XMD_2 \rightleftharpoons D_2 + XMH_2 \qquad (6)$$

the scaling factor to 0.94 and 0.90 results in calculated EIE values of 0.41 and 0.51, respectively, for X = Cl. In general, the choice of a scaling factor is not critical to the major conclusions in this work.

Inspection of the factors contributing to the EIEs given in Table II reveals that the inverse values arise from a strong normal MMI contribution (yielding a positive $\Delta S°$) offset by an even stronger inverse contribution from the combined EXC and, especially, EXP(ZPE) terms (yielding a positive $\Delta H°$). The MMI value, 5.66,[23] arises exclusively from the H_2/D_2 translational and rotational partition function ratios since the masses and moments of inertia for the metal complexes in eq 6 are not significantly altered by deuterium substitution. The inverse EXC term (0.84; X = Cl) has a substantial contribution from the M–H/M–D bending vibrations of XMH_2/XMD_2; the stretching vibrational frequencies are too high to have significantly populated excited states at moderate temperatures. The strongly inverse term EXP(ZPE) (0.10; X = Cl) results from the large and positive zero point energy difference ($\Delta\Delta$ZPE) for eq 6 (1.39 kcal/mol; X = Cl, Table II). Although the very strong H_2/D_2 bond makes a strong negative contribution to the ΔZPE (−1.83 kcal/mol), the presence of six isotope-sensitive vibrations in XMH_2/XMD_2 (Table I) produces a much larger ΔZPE term (3.22 kcal/mol) and thus makes D_2 addition to XM significantly more exothermic than H_2 addition. The important role of the four Ir–H bending modes in determining the final EIE can be demonstrated by eliminating their frequencies from the calculations in eq 4. The corresponding $\Delta\Delta$ZPE value is only 0.08 kcal/mol; the EXC and EXP(ZPE) values become 0.92 and 0.89, respectively (X = Cl), and EIE becomes normal and large: 4.6.

The inverse EIE of eq 6 (X = Cl) has been directly verified experimentally. A solution of **1** (5 mM) in benzene-d_6 under a 1:1 H_2/D_2 gas mixture (900 Torr) gives a ratio of **2**-h_2:**2**-d_2 of 0.55 (±0.06) as measured by ^1H NMR spectroscopy (eq 7; see Experimental Section); this ratio is thus the EIE of eq 1 (X = Cl; R = Ph).

$$\mathbf{1} + H_2 + D_2 \rightarrow \mathbf{2}\text{-}h_2 + \mathbf{2}\text{-}d_2 \qquad (7)$$

More revealingly, the rates of addition and elimination of H_2 and D_2 (eq 1) have been measured, by Wernke and Vaska,[15] over the temperature range of 20–40 °C. These measurements allow determination of the values of $\Delta\Delta H°$ (0.8 kcal/mol) and $\Delta\Delta S°$ (2.0 eu) of eq 1 (i.e., $\Delta H°$ and $\Delta S°$ of eq 6 for the triphenylphosphine analogue of ClM). These values (no error limits were given) are in excellent agreement with our calculated values, $\Delta\Delta H° = 1.14$ kcal/mol and $\Delta\Delta S° = 2.28$ eu, and strongly support our analysis of the individual terms from which the overall EIE value is composed.

During the course of this work, two groups independently reported similarly inverse EIEs for H_2/D_2 addition to transition-metal complexes. Rabinovich and Parkin[17] found an EIE of 0.63 at 60 °C for addition to $W(PMe_3)_4I_2$; they noted that consideration of the W–H/D bending modes was required to explain the inverse EIE. $\Delta\Delta H°$ and $\Delta\Delta S°$ values of 1.9 ± 0.9 kcal/mol and 6 ± 4 eu, respectively, were determined, consistent with our calculated values in both direction and magnitude. While the tungsten and iridium complexes are not closely related, the resulting metal–hydrogen bond strengths are similar and the apparent similarity of the isotope effects is therefore not particularly unexpected.

Hostetler and Bergman[16] reported an EIE of 0.54 (0 °C) for H_2/D_2 addition to the iridium center of $Cp_2Ta(\mu\text{-}CY_2)_2Ir(CO)PPh_3$ (Y = H/D), a system more closely related to MX. Their experimental values of $\Delta\Delta H°$ (1.0 ± 0.6 kcal/mol) and $\Delta\Delta S°$ (2.2 ± 1.8 eu) are in remarkably good agreement with our calculated values. It must be noted, however, that the experimental values reflect a composite of the primary H_2/D_2 EIE and the β-secondary EIE resulting from substitution at the Y position. (To avoid isotope scrambling during the reaction, it was necessary to measure H_2 addition to the μ-CH_2 complex and D_2 addition to the μ-CD_2 complex.)

H_2/D_2 Addition to HM: primary isotope effects. As a result of the symmetry number difference between MH_3 and *cis*-HMD_2 (2 and 1, respectively), an apparently stronger inverse EIE (0.33) is computed for eq 8, X = H, as compared with X = Cl (0.46) or Me (0.57). This effect may be viewed as resulting from the

$$H_2 + HMD_2 \rightleftharpoons D_2 + HMH_2 \qquad (8)$$

fact that, for statistical reasons, elimination of H_2 from MH_3 should be twice as fast as elimination of D_2 from *cis*-HMD_2. With the SYM term factored out, a more meaningful EIE of 0.66 is obtained.

The symmetry effect is not operative in the equilibrium involving formation of *trans*-HMD_2 (EIE = 0.73). A difference in the ZPE values between the two HMD_2 isomers (0.12 kcal/mol) reflects the stronger trans influence of a hydride ligand over that of a CO ligand; the higher frequency position is therefore trans to CO and is thus the preferred binding site for D.

H_2 Addition to HM/DM: α-Secondary Isotope Effects. The secondary α-EIE for H_2 addition to HM is the equilibrium constant of eq 9. For the formation of *cis*-DMH_2, the calculations give

$$HM + DMH_2 \rightleftharpoons DM + HMH_2 \qquad (9)$$

$K_{eq} = 0.44$. As in the case of H_2/D_2 addition to HM, a symmetry factor (SYM = 0.5) disfavors formation of HMH_2. Factoring this out gives a normalized α-EIE value of 0.88, driven essentially by the EXP(ZPE) term (0.84; $\Delta\Delta$ZPE = 0.10 kcal/mol). The inverse value reflects the preexisting Ir–H/Ir–D bond being strengthened upon addition of H_2; the Ir–D stretching frequencies in DM and *cis*-DMH_2, for example (both clearly identified by the absence of coupling with other vibrational modes), are 1436 and 1568 cm^{-1}, respectively.

For the formation of the *trans*-DMH_2 product (C_{2v} point group, $\sigma = 2$; SYM = 1), α-EIE is 0.74 ($\Delta\Delta$ZPE = 0.21 kcal/mol). The

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[23] The value ignores the rotational quantization effects. At room temperature, these contribute a factor of 1.05 and are ignored in the present calculations.

Table II. Primary and Secondary Deuterium Equilibrium Isotope Effects for Hydrogen Addition to XM; X = H, CH_3, and Cl

X	SYM	MMI	EXC	ΔΔZPE[a]	EXP(ZPE)	EIE[b]	EIE_B[c]	ΔH^0 [d]	ΔS^0 [d]
Primary EIE (eq 6)									
Cl	1.0	5.66	0.84	1.39	0.10	0.46	0.45	1.15	2.28
Me	1.0	5.66	0.83	1.25	0.12	0.57	0.57	1.01	2.27
cis-H[e]	0.5	5.66	0.80	1.18	0.14	0.33	0.33	0.93	0.81
trans-H[f]	1.0	5.66	0.79	1.06	0.17	0.74	0.73	0.80	2.09
α-Secondary EIE (eq 9)									
H/D[g]	0.5	1.00	1.04	0.10	0.84	0.44	0.44	0.10	−1.28
H/D[h]	1.0	1.00	1.06	0.21	0.70	0.74	0.75	0.24	0.19
β-Secondary EIE (eq 10)									
CH_3/CD_3	1.0	1.00	1.02	0.10	0.84	0.86	0.86	0.11	0.06

[a] In kcal/mol. [b] Computed at 300 K, using eq 4. [c] Computed at 300 K, using the Bigeleisen expression, eq 5. [d] ΔH^0 in kcal/mol and ΔS^0 in eu. Values obtained from the plot of computed ln(EIE) versus $1/T$ in the temperature range of 280–320 K. [e] *cis*-HMD_2, H cis to CO, $\sigma = 1$. [f] *trans*-HMD_2, H trans to CO, $\sigma = 2$. [g] *cis*-DMH_2, D cis to CO in the dihydride product, $\sigma = 1$. [h] *trans*-DMH_2, D trans to CO in the dihydride product, $\sigma = 2$.

Table III. Primary and Secondary Deuterium EIE for Methane Addition to XM; X = H

substrate	SYM	MMI	EXC	ΔΔZPE[a]	EXP(ZPE)	EIE[b]	EIE_B[c]	ΔH^0 [d]	ΔS^0 [d]
Primary C–H EIE (eqs 11–13)									
CH_4/CH_3D	4.0	1.48	0.93	−0.21	1.42	7.77	7.64	−0.30	3.06
CH_4/CD_4	1.0	3.95	0.73	−0.14	1.26	3.64	2.42	−0.38	1.29
α-Secondary EIE (eq 14)									
cis-CH_4[e]	1.0	1.00	1.06	0.14	0.79	0.84	0.84	0.15	0.13
trans-CH_4[f]	1.0	1.00	1.08	0.25	0.66	0.71	0.71	0.28	0.24

[a] In kcal/mol. [b] Computed at 300 K, using eq 4. [c] Computed at 300 K, using the Bigeleisen expression, eq 5. [d] ΔH^0 in kcal/mol and ΔS^0 in eu. Values obtained from the plot of computed ln(EIE) versus $1/T$ in the temperature range of 280–320 K. [e] Cis CH_4 addition to DM, D cis to CO in the product. [f] Trans CH_4 addition, D retained trans to CO in the product.

more inverse isotope effect is due to the lower zero point energy (0.11 kcal/mol) of the *trans*-DMH_2 isomer. As in the case of the *cis*-HMD_2 complex, this is due to occupation by D of the higher frequency position trans to CO.

The primary EIE for H_2/D_2 addition to HM (eq 8) is similar to the secondary EIE for H_2 addition to HM/DM (eq 9); in particular, for formation of the trans products, the value is 0.74 in both cases. This is purely coincidental, however, and results only from our choice of temperature (300 K). The primary EIE of eq 8 (X = H) is dominated by a large ΔΔZPE term overcompensating the large entropy terms and is thus highly temperature dependent, unlike the secondary EIE of eq 9. For example, at 400 K, the respective values of the primary and secondary EIEs are 1.01 (i.e., normal) and 0.81.

H_2 Addition to CH_3M/CD_3M: β-Secondary Isotope Effects. Deuteration of the methyl ligand of $(CH_3)M$ allows determination of the β-secondary isotope effect on the addition of H_2.

$$(CH_3)M + (CD_3)MH_2 \rightleftharpoons (CD_3)M + (CH_3)MH_2 \quad (10)$$

The equilibrium constant for eq 10, β-EIE, has a value of 0.86; the major factor in this case is EXP(ZPE) = 0.84. The inverse value indicates that the C–H/C–D bonds of the methyl ligand are strengthened by H_2 addition to the iridium center. The calculated vibrational frequencies of the methyl group are indeed markedly larger in $(CH_3)MH_2$ than in $(CH_3)M$. In particular, the C–H stretching frequencies (unscaled) shift from 3082, 3148, and 3163 cm^{-1} in $(CH_3)M$ to 3106, 3162, and 3213 cm^{-1} in $(CH_3)MH_2$. A plausible cause of the change in C–H bond strength is a reduced Ir–CH_3 repulsive π-interaction in the Ir(III) product relative to that of the Ir(I) reactant (cf. ν_{CO} = 1954 and 1982 cm^{-1} for **1** and **2**, respectively).

Hostetler and Bergman have estimated an inverse β-secondary EIE of 0.74 for R_3Si–H addition to $Cp_2Ta(\mu\text{-}CY_2)_2Ir(CO)PPh_3$ (Y = H/D) on the basis of a composite value which included the primary EIE for Si–H/Si–D addition.[16,24] For MeI addition to $Ir(PPh_3)_2(CO)X$ (X = CH_3/CD_3), they found an inverse KIE of 0.922. Both of these experimental results, in accord with our calculations, indicate that β-deuterium substitution favors oxidation of the iridium(I) center.

Methane Addition to HM: C–H/C–D Primary Isotope Effects. The EIE has been determined for CH_4/CH_3D and CH_4/CD_4 addition to HM, eqs 11 and 12 (Table III).

$$CH_4 + HM(CH_3)D \rightleftharpoons CH_3D + HM(CH_3)H$$

$$K = 7.77 \text{ (1.94 per bond)} \quad (11)$$

$$CH_4 + HM(CD_3)D \rightleftharpoons CD_4 + HM(CH_3)H$$

$$K = 3.64 \text{ (3.64 per bond)} \quad (12)$$

Unlike H_2 addition products, all the C–H addition products, $(H_3C)MH_2$, have the same number of vibrational modes directly sensitive to isotope labeling as does the reactant (methane). Since the methane C–H bond is stronger than the Ir–H bond, ΔΔZPE values for eqs 11 and 12 are negative (−0.21 and −0.14 kcal/mol, respectively), i.e., C–H addition is energetically favored over C–D addition. Factoring out the symmetry ratio for eq 11 (CH_4/CH_3D) reveals that the EIE per C–H/C–D bond is 1.94, composed of an MMI term of 1.48 and a vibrational term of 1.32 (EXC = 0.93, EXP(ZPE) = 1.42). An EIE of approximately 1.3 would therefore be predicted for oxidative addition of a large alkane (i.e., one with no significant MMI term) RH/RD, where R has no other isotopically labeled substituents (i.e., secondary isotope effects are absent). The calculation of a normal EIE for C–H addition is in good agreement with observed isotopic intramolecular equilibria for RH/RD addition products (R = Me[25,26] or Ph[27]) which establish the greater preference of D for the carbon-bound position.

Replacing CH_3D by CD_4 (i.e., eq 12 versus eq 11) results in a large increase in the (per bond) EIE, K_{CH_4}/K_{CD_4} = 3.64, resulting essentially from a large MMI term (3.95). This is partially canceled by a strongly inverse EXC term of 0.73, resulting from the presence of very low-energy C–H/C–D) bending frequencies in the methyl complex which are absent in methane.

CH_4 Addition to HM/DM: α-Secondary Isotope Effects. The α-secondary EIE for methane addition to HM/DM, eq 13, is 0.84 for cis addition (yielding the isomer with D cis to CO). This value is similar to that computed for cis H_2 addition (0.88 after

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$$HM + DM(CH_3)H \rightleftharpoons DM + HM(CH_3)H \qquad (13)$$

normalization). For trans addition of methane (yielding the isomer with D trans to CO), the EIE is 0.71 as compared with 0.74 for trans addition of H_2 (keeping D trans to CO). In both cases, the isomerization placing D trans to CO (versus trans to CH_3 or H, respectively) is favored by a contribution to $\Delta\Delta ZPE$ of -0.11 kcal/mol.

Computational Details

All the ab initio electronic structure calculations were carried out using the Gaussian 90 series of programs[28] on a CRAY YMP/832 at the Pittsburgh Supercomputer Center or on a Convex C220 minisupercomputer at Rutgers University. Effective core potentials (ECPs) and corresponding valence electron basis sets developed by Ermler, Christiansen, and co-workers were employed for all non-hydrogen atoms.[29,30] In previous work, we and others have found these potentials accurate and reliable in describing the electronic and structural properties pertaining to a variety of complexes.[31] Of the two ECP types available for Ir, only the larger core type containing 68 electrons has been used. The appropriateness of using this ECP in the present systems has been examined and justified in detail elsewhere.[11,32] The valence basis sets were contracted into at least double-ζ quality as follows: $(4s,4p) \rightarrow [3,1/3,1]$ for C, O, P, and Cl; and $(3s,3p,3d) \rightarrow [1,1,1/2,1/3,1]$ for Ir (six Cartesian d functions). Hydrogens bonded to Ir, C, and P were described by 311G,[33] 21G,[34] and STO-3G[35] basis sets, respectively. Geometries were fully optimized within appropriate symmetry constraints (C_s or C_{2v}) at the restricted closed-shell Hartree–Fock level using energy gradient methods. Vibrational frequencies were obtained by finite differences of analytically computed first derivatives. Some complexes had one or two low lying imaginary frequencies corresponding to PH_3 and CH_3 rotations. These modes were insensitive to isotope substitution and ignored in the calculations.

Experimental Section

Vaska's complex was prepared according to published methods.[36] NMR spectra were recorded on a 400-MHz Varian spectrometer. A 5 mM solution of **1** in benzene-d_6 was sealed in an NMR tube under 900 Torr of a 1:1 H_2:D_2 mixture. Under these conditions, the EIE is the concentration ratio of [**2**-h_2] to [**2**-d_2], R_{obs}, attained at equilibrium. A reference sample containing 900 Torr H_2 was similarly prepared. The concentration of all product species [$\mathbf{2}_{tot}$] (including HD complexes) was taken as $^1/_{12}$ the integrand of the PPh_3 ortho phenyl hydrogens (δ 7.91). [**2**-h_2] was determined using the integrand of the low-field hydride peak (corresponding to H trans to CO) (δ -6.67, td, $^2J_{P-H} = 17.0$ Hz, $^2J_{H-H} = 4.5$ Hz), [H_{obs}]. The upfield hydride peak was not used because the hydrides of **2**-h_2 and **2**-dh were not resolved (*vide infra*). The spectra of the reference sample showed that [H_{obs}] was always about 4% larger than expected on the basis of the stoichiometry of the ortho phenyl hydrogens (delay time = 20 s). Except for additional small peaks corresponding to newly formed HD gas from the catalytic exchange between H_2 and D_2 by Vaska's complex,[37] the initial spectrum in the experiment (1.5 h) was almost identical to the reference spectrum outside of the hydride region; accordingly, 0.96[H_{obs}] was taken as proportional to [**2**-h_2]. [**2**-d_2] was then estimated by subtracting [**2**-h_2] from [$\mathbf{2}_{tot}$], which gave an initial R_{obs} value of 1.2 (as expected on the basis of the kinetic isotope effect). Resonances attributable to $HDIr(PPh_3)_2(CO)Cl$ complexes became apparent in the spectra after ca. 6 h of reaction time. The ratio of the ortho phenyl hydrogens to the combined meta plus para hydrogens, however, did not change throughout the experiment, indicating that the use of the ortho H integrand as a reference for the total concentration of products is valid.[38] In the downfield hydride region, a peak 0.015 ppm higher than (overlapping with) that of **2**-h_2 (t, $^2J_{P-H} = 17.0$ Hz), corresponding to the HD complex with H trans to CO (**2**-hd), occupied 20–25% of the total M–H region after 16–45 h, as estimated by spin simulation (LAME program). Using these percentages, we resolved the scaled [H_{obs}] into [**2**-h_2] and [**2**-hd]. Assuming the concentration of the HD complex isomer with D trans to CO [**2**-dh] is equal to [**2**-hd], then R_{obs} = [**2**-h_2]/([$\mathbf{2}_{tot}$]–[**2**-d_2]–2[**2**-hd]) with values of 0.52 and 0.58 at 30 and 45 h, respectively. EIE was taken as the average, 0.55 ± 0.06 (ambient temperature).

Conclusions

Primary and secondary isotope effects for the addition of hydrogen and methane to $Ir(PH_3)_2(CO)X$ (X = Cl, CH_3, and H) have been calculated and decomposed according to standard thermodynamic expressions (eq 4). For H_2/D_2 addition, a strongly inverse EXP(ZPE) term (0.10 at 300 K for X = Cl) results from a product with six isotope-sensitive frequencies (four bending and two stretching modes) being formed from a reactant (H_2/D_2) containing only one such mode. This contribution to the reaction enthalpy is largely canceled by the MMI term (5.66) and an entropic factor, and the resulting primary EIEs for H_2/D_2 addition are only moderately inverse (0.46–0.74). For CH_4/CD_4 addition, a large MMI term (3.95) is unmitigated by the EXP(ZPE) term; this results in a large EIE (3.64). Calculated secondary α- and β-EIEs, resulting from deuteration of X (H or CH_3, respectively), favor the addition of hydrogen or methane. These secondary EIEs arise because the Ir(III) products possess Ir–H or IrC–H bonds which are stronger (higher frequency) than those of the respective Ir(I) reactants.

The present set of calculations extends the applicability of ab initio electronic structure methods to the determination of the several factors contributing to equilibrium isotope effects in organometallic reactions. The analysis of our computed results has widespread applicability, and we believe further applications of these techniques will be of great assistance in the analysis of multistep reactions where vibrational frequencies of intermediates are not available.

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Supplementary Material Available: Tables containing Z-matrices, frequency values, and vector components of all the normal modes for $ClMH_2$ and $ClMD_2$ (14 pages). Ordering information is given on any current masthead page.

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