$PhSCH_2COCH_3$ in 40% yield: mp 36–38 °C (lit.[37] mp 34–35 °C); ^1H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 3.65 (s, 2 H), 7.14–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 28.01, 44.65, 126.84, 129.17, 129.47, 134.63, 203.61.

α-(Phenylseleno)acetophenone ($PhSeCH_2COPh$). The compound was prepared according to the procedure of Detty and Wood.[38] After distillation, the residual oil was found to be contaminated with a small amount of diphenyl diselenide. The impurity was removed by flash chromatography using pentane as the eluent. The selenium compound was eluted with diethyl ether and recrystallized from methanol to give white crystals of $PhSeCH_2COPh$: mp 42–44 °C (lit.[38] bp 162–164 °C, 0.8 mmHg); ^1H NMR ($CDCl_3$) δ 4.20 (s, 2 H), 7.31–7.56 (m, 8 H), 7.85–7.93 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.85, 127.99, 128.52, 128.60, 129.06, 129.15, 133.18, 133.88, 135.27, 194.71.

Bis(phenylthio)acetophenone ($(PhS)_2CHCOPh$). A mixture of 40 mmol of *N*-chlorosuccinimide and 40 mmol of α-(phenylthio)acetophenone in 100 mL of CCl_4 was refluxed for 30 min and then allowed to stir at room temperature for 6 h. After filtration, the solvent was removed under vacuum, and the oil residue was used without further purification in the preparation of bis(phenylthio)acetophenone: ^1H NMR ($CDCl_3$) δ 6.42 (s, 1 H), 7.20–7.65 (m, 8 H), 7.89–8.10 (m, 2 H).

A solution of α-chloro-α-(phenylthio)acetophenone (25 mmol) in 100 mL of methanol was added to a methanolic solution of sodium benzenethiolate under argon. After the normal workup, the oil residue was recrystallized repeatedly from methanol to provide bis(phenylthio)acetophenone in 50% yield: mp 101–103 °C (lit.[39] mp 99–100 °C); ^1H NMR ($CDCl_3$) δ 5.74 (s, 1 H), 7.25–7.62 (m, 13 H), 7.92–7.96 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 62.71, 128.54, 128.72, 128.985, 129.01, 132.21, 133.47, 133.86, 134.32, 191.21.

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Secondary β-Deuterium Isotope Effects on the Rates and Equilibria of Organometallic Oxidative Addition/Reductive Elimination Reactions

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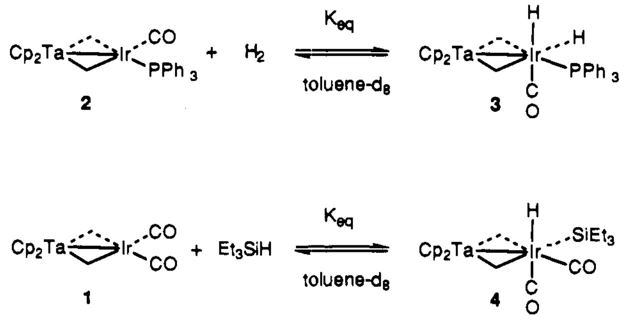
Abstract: We report a study of β-deuterium isotope effects on the rate and equilibrium of an organometallic transformation: the oxidative addition of silane R_3SiH (R = Et) and the corresponding deuteride R_3SiD to the iridium center in the heterodinuclear complex $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ (**1**) and to its tetradeuterated analogue $Cp_2Ta(\mu\text{-}CD_2)_2Ir(CO)_2$ (**1-*d*$_4$**). The Si–H(D) bond contributes only a small normal isotope effect to the forward rate constant k_1 ($k_1^H/k_1^D = 1.13 \pm 0.06$). An *inverse* effect ($k_1^H/k_1^D = 0.875 \pm 0.022$) is caused by isotopic tetrasubstitution at the bridging methylenes. For the reductive elimination of Et_3SiX from $Cp_2Ta(\mu\text{-}CX_2)_2Ir(X)(SiEt_3)(CO)_2$ (X = H, D), the Si–H(D) bond again contributes a small normal isotope effect to the rate constant k_{-1} ($k_{-1}^H/k_{-1}^D = 1.45 \pm 0.08$). However, a *normal* effect ($k_{-1}^H/k_{-1}^D = 1.25 \pm 0.03$) is caused by the secondary isotopic substitution. The combined primary and secondary *equilibrium* isotope effect on the silane oxidative addition/reductive elimination equilibrium constant $K_{eq}^H/K_{eq}^D = [k_1/k_{-1}]^H/[k_1/k_{-1}]^D$ is 0.53 ± 0.04 at 0 °C. A kinetic isotope effect analogous to that observed with **1** is measured for the oxidative addition of methyl iodide to $(PPh_3)_2Ir(CO)(CX_3)$ (X = H, D) ($k_1^H/k_1^D = 0.922 \pm 0.030$ in THF at 0 °C). This suggests that the inverse β-deuterium isotope effect on oxidative addition is a general phenomenon. Kinetic isotope effects of similar direction and magnitude were also observed for oxidative addition of CH_3I ($k_1^H/k_1^D = 0.752 \pm 0.018$ in THF at 0 °C) and Ph_3SiH ($k_1^H/k_1^D = 0.898 \pm 0.077$ in THF at 10 °C) to the tantalum/iridium complex **1**, indicating that steric effects are not the source of the measured difference in rate behavior. The tendency of deuterium to act as an inductive electron donor relative to hydrogen is suggested to account for its ability to enhance the rate of oxidative addition reactions that convert iridium(I) to iridium(III).

The use of isotope effects to study the mechanism of organic reactions is a well-established technique.[1,2] Primary hydrogen/deuterium isotope effects are in general the most straightforward to interpret, usually indicating the degree of C–H bond-breaking in the transition state. On the other hand, secondary isotope effects (SIE)[3] and their analyses[4-6] are still the basis for active research. Their proper interpretation requires extensive experimentation in order to properly describe their effect on a reaction.

Scheme I



This ambiguity results from the number of ways in which SIEs (any or all of which may be operating simultaneously) have been proposed to act: (1) by hyperconjugative interaction of the β-C–H bond with a developing intermediate carbocation; (2) by a change

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Table I. Equilibrium Data for the System H_2 + $Cp_2Ta(CH_2)_2Ir(CO)(PPh_3)$ (**2**) $\rightleftharpoons$ $Cp_2Ta(CH_2)_2Ir(H)_2(CO)(PPh_3)$ (**3**) in Toluene-d_8

T (K)	$[H_2]$ (M)[a]	[**2**] (M)	[**3**] (M)	K_{eq} (M^{-1})[b]
295	2.75×10^{-3}	1.61×10^{-4}	2.32×10^{-3}	5240
296	2.75×10^{-3}	1.66×10^{-4}	2.31×10^{-3}	5060
308	2.85×10^{-3}	3.47×10^{-4}	2.13×10^{-3}	2150
308	3.09×10^{-3}	3.47×10^{-4}	2.13×10^{-3}	1990
323	3.40×10^{-3}	6.00×10^{-4}	1.88×10^{-3}	922
323	3.39×10^{-3}	6.15×10^{-4}	1.86×10^{-3}	892
338	3.89×10^{-3}	9.52×10^{-4}	1.53×10^{-3}	413
338	3.95×10^{-3}	9.82×10^{-4}	1.50×10^{-3}	387
353	4.63×10^{-3}	1.39×10^{-3}	1.09×10^{-3}	170
353	4.84×10^{-3}	1.40×10^{-3}	1.08×10^{-3}	159

[a] Determined by integration of the signal vs ferrocene in the ^1H NMR spectrum. [b] The error limits for K_{eq} were estimated to be ±3% on the basis of the reproducibility of the values.

in hybridization at the reactive center during the reaction; (3) by steric effects, due to the larger vibrational amplitude of the C–H bond relative to the C–D bond; (4) by inductive effects, because deuterium is a better electron donor than hydrogen. To further complicate matters, the directions of these effects can be at variance with each other.

Isotope effects on the reactions of organometallic complexes have been much less extensively studied. Several important papers have reported the primary isotope effect for oxidative additions,[7-9] reductive eliminations,[10,11] and hydrogen transfer reactions.[12] In addition, others have studied isotope effects on agostic interactions[13] and insertions into M–H bonds.[14,15] There has also been some work on SIEs for organometallic transformations, such as the α-effect on the rate of the oxidative addition of MeI[16] and the cleavage of C–O bonds of ferrocenylmethyl benzoate.[17] However, until recently, studies on the β-isotope effect for organometallic reactions were nearly nonexistent.[18,19]

Herein we report that a change of isotope at a position β to the reacting metal center can alter not only the equilibrium constant for the reaction of $Cp_2Ta(CH_2)_2Ir(CO)_2$ (**1**) with Et_3SiH (Scheme I) but also the rate of the oxidative addition and reductive elimination reaction involved in this equilibrium. In addition, we describe how this SIE influences the rate of oxidative addition of methyl iodide to a number of iridium complexes. We propose that these observations may be a general and useful tool for mechanistic studies on organometallic compounds.

Results

Equilibrium Studies. The reaction of H_2 with $Cp_2Ta(CH_2)_2Ir(CO)(PPh_3)$ (**2**) leads to the oxidative addition product $Cp_2Ta(CH_2)_2Ir(H)_2(CO)(PPh_3)$ (**3**) in which dihydrogen adds regioselectivity above the Ir–CO bond (Scheme I).[20,21] In toluene-d_8, **2**, **3** and H_2 are the only detectable species over a wide range of temperatures. The other isomer of **3**, in which H_2 adds above the Ir–PPh_3 bond, has not been detected. From the plot of ln K_{eq} vs T^{-1}, the enthalpy of reaction, $\Delta H° = -12.0 \pm 0.2$ kcal/mol, and the entropy of reaction, $\Delta S° = -23.7 \pm 0.6$ eu, were calculated (Table I). From this $\Delta H°$ and the bond dissociation energy (BDE) of H_2 (104.2 kcal/mol),[22] the average BDE for the Ir–H bonds in **3**, 58.1 ± 0.2 kcal/mol, was derived.

Table II. Equilibrium Data for the System D_2 + $Cp_2Ta(CD_2)_2Ir(CO)(PPh_3)$ (**2-*d*₄**) $\rightleftharpoons$ $Cp_2Ta(CD_2)_2Ir(D)_2(CO)(PPh_3)$ (**3-*d*₆**) in Toluene-d_8

T (K)	$[D_2]$ (M)	[**2-d_4**] (M)	[**3-d_6**] (M)	K_{eq} (M^{-1})[a]
294.5	2.77×10^{-3}	8.84×10^{-5}	2.40×10^{-3}	9800
308	3.02×10^{-3}	2.21×10^{-4}	2.27×10^{-3}	3400
323	3.45×10^{-3}	4.18×10^{-4}	2.07×10^{-3}	1440
338	3.99×10^{-3}	7.32×10^{-4}	1.76×10^{-3}	603
353	4.84×10^{-3}	1.22×10^{-3}	1.27×10^{-3}	215

[a] The error limits for K_{eq} were estimated to be ±8% on the basis of the reproducibility of the values and the uncertainty in $[D_2]$.

Table III. Equilibrium Data for the System Et_3SiH + $Cp_2Ta(CH_2)_2Ir(CO)_2$ (**1**) $\rightleftharpoons$ $Cp_2Ta(CH_2)_2Ir(H)(SiEt_3)(CO)_2$ (**4**) in Toluene-d_8

T (K)	$[Et_3SiH]$ (M)	[**1**] (M)	[**4**] (M)	K_{eq} (M^{-1})[a]
253	1.16×10^{-3}	9.50×10^{-4}	1.13×10^{-2}	10200
273	1.60×10^{-3}	1.40×10^{-3}	1.09×10^{-2}	4870
293	3.55×10^{-3}	3.35×10^{-3}	8.95×10^{-3}	753
313	5.76×10^{-3}	5.56×10^{-3}	6.74×10^{-3}	210
333	8.29×10^{-3}	8.09×10^{-3}	4.21×10^{-3}	62.8
343	9.06×10^{-3}	8.86×10^{-3}	3.44×10^{-3}	42.8

[a] The error limits for K_{eq} were estimated to be ±4% on the basis of the reproducibility of the values.

Table IV. Equilibrium Data for the System Et_3SiD + $Cp_2Ta(CD_2)_2Ir(CO)_2$ (**1-*d*₄** $\rightleftharpoons$ $Cp_2Ta(CD_2)_2Ir(D)(SiEt_3)(CO)_2$ (**4-*d*₅**) in Toluene-d_8

T (K)	$[Et_3SiH]$ (M)	[**1-d_4**] (M)	[**4-d_5**] (M)	K_{eq} (M^{-1})[a]
273	6.55×10^{-4}	1.76×10^{-3}	1.05×10^{-2}	9110
293	2.35×10^{-3}	3.45×10^{-3}	8.84×10^{-3}	1090
313	4.49×10^{-3}	5.59×10^{-3}	6.71×10^{-3}	267
333	6.18×10^{-3}	7.91×10^{-3}	4.39×10^{-3}	81.5

[a] The error limits for K_{eq} were estimated to be ±9% on the basis of the reproducibility of the values and the uncertainty in $[Et_3SiD]$.

The equilibrium constant as a function of temperature was also measured for the analogous deuterated system, D_2, $Cp_2Ta(CD_2)_2Ir(CO)(PPh_3)$ (**2-*d*₄**) and $Cp_2Ta(CD_2)_2Ir(D)_2(CO)(PPh_3)$ (**3-*d*₆**) in toluene-d_8. Again, only one product is observed, in which D_2 oxidatively adds over the Ir–CO bond. From the plot of ln K_{eq} vs T^{-1}, the values $\Delta H° = -13.0 \pm 0.4$ kcal/mol and $\Delta S° = -25.9 \pm 1.2$ eu were calculated (Table II). The average BDE for the Ir–D bonds in **3-*d*₆**, 59.5 ± 0.4 kcal/mol, was derived from this enthalpy and the bond dissociation energy (BDE) of D_2 (106.0 kcal/mol).[22]

The equilibrium isotope effect ($K_{eq}{}^H/K_{eq}{}^D = K_{H/D}$, or EIE) for these two systems is inverse. Interestingly, the magnitude changes over the temperature range studied, from $K_{H/D} = 0.54 \pm 0.04$ at 0 °C to $K_{H/D} = 0.76 \pm 0.06$ at 80 °C. The contributions to the EIE come from both the enthalpic and entropic terms, $\Delta\Delta H°$ ($\Delta H°_D - \Delta H°_H$) = -1.0 ± 0.6 kcal/mol and $\Delta\Delta S°$ ($\Delta S°_D - \Delta S°_H$) = -2.2 ± 1.8 eu. The iso-isotopic temperature, at which the equilibrium constants are equal, is predicted to be ~180 °C. It was not possible to measure K_{eq} for the mixed isotope systems $H_2/Cp_2Ta(CD_2)_2Ir(CO)(PPh_3)$ or $D_2/Cp_2Ta(CH_2)_2Ir(CO)(PPh_3)$ because exchange between the methylene bridge protons and the $H_2(D_2)$ occurs at a rapid rate.[20]

The equilibrium constant as a function of temperature was also measured for the reaction of Et_3SiH with $Cp_2Ta(CH_2)_2Ir(CO)_2$ (**1**) to form $Cp_2Ta(CH_2)_2Ir(H)(SiEt_3)(CO)_2$ (**4**) in toluene-d_8. (Silanes do not appear to form detectable amounts of oxidative

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addition product with $Cp_2Ta(CH_2)_2Ir(CO)(PPh_3)$). Only a single isomer was seen by ^1H NMR spectrometry (Scheme I). From the plot of ln K_{eq} vs T^{-1}, the values $\Delta H° = -11.2 \pm 0.2$ kcal/mol and $\Delta S° = -25.0 \pm 0.6$ eu were calculated (Table III).

As in the case of the hydrogen systems, the reaction of Et_3SiD with $Cp_2Ta(CD_2)_2Ir(CO)_2$ (**1-d_4**) to form $Cp_2Ta(CD_2)_2Ir(D)(SiEt_3)(CO)_2$ (**3-d_5**) in toluene-d_8 was also investigated. Again, only a single isomer was seen by ^1H NMR spectroscopy. From the plot of ln K_{eq} vs T^{-1}, the values $\Delta H° = -14.1 \pm 0.4$ kcal/mol and $\Delta S° = -33.8 \pm 1.2$ eu were determined (Table IV).

The equilibrium isotope effect for these two systems is also inverse. Likewise, the magnitude of the EIE changes over the temperature range studied from $K_{H/D} = 0.53 \pm 0.04$ at 0 °C to $K_{H/D} = 0.77 \pm 0.06$ at 60 °C. Contributions to the EIE come from both the enthalpic and entropic terms, $\Delta\Delta H° = -2.9 \pm 0.6$ kcal/mol and $\Delta\Delta S° = -8.8 \pm 1.8$ eu.

Like H_2, Et_3SiH not only oxidatively adds to the iridium center but also exchanges its hydrogen with the hydrogens of the bridging methylene groups,[23] and thus data could not be obtained from the mixed systems, Et_3SiH/**1-d_4** and Et_3SiD/**1**, by ^1H NMR spectrometry. The equilibrium constants could be measured by UV/vis spectroscopy (which allows for faster measurements because nuclear relaxation is not a factor). However, because only **1**/**1-d_4** has a strong absorption in the UV/vis spectrum, values of K_{eq} had a large error associated with them and were not used.

An alternative way of obtaining the primary isotopic contribution to $K_{H/D}$ for the mixed systems is by calculating the value from the absorbances in the infrared spectrum using eq 1,[24] where

$$K_{H/D} = \Pi \exp[+1/2(u_{iAH} - u_{iAD})]\Pi \exp[-1/2(u_{iBH} - u_{iBD})] \qquad (1)$$

$u_i = hc\nu_i/kT$ is the energy of the vibration, h is Planck's constant, c is the speed of light, ν_i is the frequency of the normal mode i, k is the Boltzmann constant, and T is the temperature, in this case 273 K.

After assigning the Si-H/Si-D and the Ir-H/Ir-D IR frequencies, these values were used to calculate the contributions to $K_{H/D}$ from the primary isotope effect. By assuming $K_{H/D}$(total) = $K_{H/D}$(primary)$K_{H/D}$(secondary), the secondary effect was estimated.

For the primary vibrational changes summarized in eq 2, the following IR vibrational stretching frequencies were used: ν_{iAH}

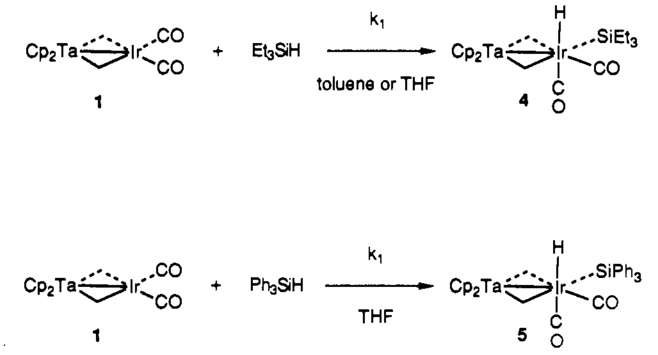
$$\text{Ir-D} + \text{Si-H} \overset{K_{H/D}}{\rightleftharpoons} \text{Ir-H} + \text{Si-D} \qquad (2)$$

$\equiv \nu(\text{Si-H}) = 1978\ \text{cm}^{-1}$, $\nu_{iAD} \equiv \nu(\text{Si-D}) = 1494\ \text{cm}^{-1}$, $\nu_{iBH} \equiv \nu(\text{Ir-H}) = 2095\ \text{cm}^{-1}$ and $\nu_{iBD} \equiv \nu(\text{Ir-D}) = 1600\ \text{cm}^{-1}$.

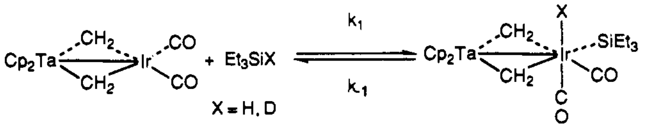
Using eq 1, a value for $K_{H/D}$(stretching) ≈ 0.97 was obtained. There is also a significant contribution to $K_{H/D}$ from the bending vibrations. The following frequencies were used for this calculation: $\sigma_{iAH} \equiv \sigma(\text{Si-H}) = 860\ \text{cm}^{-1}$, $\sigma_{iAD} \equiv \sigma(\text{Si-D}) = 619\ \text{cm}^{-1}$, $\sigma_{iBH} \equiv \sigma(\text{Ir-H}) = 1016\ \text{cm}^{-1}$, and $\sigma_{iBD} \equiv \sigma(\text{Ir-D}) = 720\ \text{cm}^{-1}$. The value for σ(Si-H) was taken from a full vibrational study for Me_3SiH.[25] The value for σ(Ir-H) was chosen on the basis of similarities observed in the IR spectra for the products of three different silane (Ph_3SiH, Et_3SiH, and Me_3SiH) oxidative additions onto **1**. The frequencies for the σ(X-D) bending vibrations were estimated by dividing σ(X-H) by 1.39 (Si-H) or by 1.41 (Ir-H) (the corrected[22] reduced mass).

Two bending vibrations are associated with each bond, the in-plane bend and the out-of-plane bend. These are degenerate for Et_3SiH and are assumed degenerate for the Ir-H bond. The latter seems valid since the energy for the bending vibration depends mainly on the steric environment about the bond. Therefore, from these IR values, a $K_{H/D}$(bending) ≈ (0.87)(0.87) ≈ 0.76 was obtained. An approximate value for the total primary (SiH → IrH) EIE can be calculated as follows: $K_{H/D}$(primary) = $K_{H/D}$(stretching)$K_{H/D}$(bending) ≈ 0.73. Using this value, the secondary isotope contribution to the EIE due to the bridging CH_2 groups can be derived: $K_{H/D}$(secondary) = $K_{H/D}$(total)/$K_{H/D}$(primary) = 0.74.

Scheme II



Scheme III. Primary Isotope Effect Results



$K_{H/D} = 0.78$ (from IR calculation)

$k_{1\,(H/D)} = 1.13$ (from UV/Vis measurement)

$k_{-1\,(H/D)} = k_1/K_{eq} = 1.45$

Kinetic Studies

Reactions with Silanes. With the equilibrium isotope effects in hand, we turned to a determination of the effect of deuteration on the rates of the forward and reverse reactions in Scheme I. The dihydrogen system was not amenable to this analysis due to the low solubility of hydrogen in most solvents and the tendency for the rate of hydrogen diffusion into the solvent to be the rate determining step. Thus, a detailed study was performed on the rate of oxidative addition of Et_3SiH/Et_3SiD to **1** and **1-d_4** (Scheme II). Fortunately, at relatively high silane concentrations and low temperatures the rates were much faster than the rate of IrH/CH_2 exchange, and thus mixed systems could be studied. UV/vis spectrometry was a useful tool for this purpose because it provided high accuracy and because the starting materials were yellow and the products colorless. The observed KIEs were small, and so each rate was measured 3 to 4 times (see Table V for all measured rate constants and their standard deviations). As a double-check, the loss or gain of an additional band in the UV region of the spectrum was monitored.

The rate of oxidative addition of Et_3SiX to **1** was found to be first order in silane and first order in **1**. For example, the oxidative addition of Et_3SiH to **1** in toluene has a second-order rate constant of $2.15 \pm 0.06\ \text{M}^{-1}\ \text{s}^{-1}$ at −7.8 °C. The analogous addition of Et_3SiH to **1-d_4** has a second-order rate constant of 2.47 ± 0.06. Thus, the secondary KIE due to the bridging CH_2 groups, $k_H/k_D = 0.874 \pm 0.032$, is inverse. The effect due to each deuterium is $(0.874)^{1/4} = 0.967$. These two reactions were also run at 0 °C in order to detect any temperature dependence on the KIE (higher temperatures could not be studied because of competitive hydride–methylene exchange in the mixed systems). The second-order rate constant for the addition to **1** was $3.72 \pm 0.07\ \text{M}^{-1}\ \text{s}^{-1}$ and to **1-d_4**, $4.25 \pm 0.07\ \text{M}^{-1}\ \text{s}^{-1}$. This gave a secondary KIE of 0.875 ± 0.022, identical to that measured at −7.8 °C.

The addition of Et_3SiD to both **1** and **1-d_4** in toluene at 0 °C was also monitored in order to measure the primary contribution

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Table V. Comparison of Kinetic Isotope Effects

system	k_H (M^{-1} s^{-1})	k_D (M^{-1} s^{-1})	k_H/k_D
1/Et_3SiH in THF at 0 °C[a]	2.79 ± 0.04		
1-d_4/Et_3SiH in THF at 0 °C		3.15 ± 0.08	0.886 ± 0.026
1/Et_3SiD in THF at 0 °C[b]	2.66 ± 0.08		
1-d_4/Et_3SiD in THF at 0 °C		3.05 ± 0.08	0.872 ± 0.035
1/Et_3SiH in toluene at −7.8 °C	2.15 ± 0.06		
1-d_4/Et_3SiH in toluene at −7.8 °C		2.47 ± 0.06	0.874 ± 0.032
1/Et_3SiH in toluene at 0 °C	3.72 ± 0.07		
1-d_4/Et_3SiH in toluene at 0 °C		4.25 ± 0.07	0.875 ± 0.022
1/Et_3SiD in toluene at 0 °C	3.30 ± 0.18		
1-d_4/Et_3SiD in toluene at 0 °C		3.77 ± 0.18	0.875 ± 0.063
1/Ph_3SiH in THF at 10 °C	1.32 ± 0.07		
1-d_4/Ph_3SiH in THF at 10 °C		1.47 ± 0.10	0.898 ± 0.077
1/CH_3I in THF at 0 °C	(1.03 ± 0.02) × 10^{-2}		
1-d_4/CH_3I in THF at 0 °C		(1.37 ± 0.02) × 10^{-2}	0.752 ± 0.018
1/CH_3I in THF at 10 °C	(2.20 ± 0.01) × 10^{-2}		
1-d_4/CH_3I in THF at 10 °C		(2.54 ± 0.11) × 10^{-2}	0.866 ± 0.038
1/CH_3I in THF at 20 °C	(4.53 ± 0.14) × 10^{-2}		
1-d_4/CH_3I in THF at 20 °C		(4.98 ± 0.14) × 10^{-2}	0.910 ± 0.038
1/CH_3I in THF at 30 °C	(9.41 ± 0.53) × 10^{-2}		
1-d_4/CH_3I in THF at 30 °C		(10.4 ± 0.52) × 10^{-2}	0.905 ± 0.067[c]
1/CH_3I in THF at 40 °C	(1.64 ± 0.11) × 10^{-1}		
1-d_4/CH_3I in THF at 40 °C		(1.75 ± 0.08) × 10^{-2}	0.937 ± 0.076
7/CH_3I in THF at 0 °C	(2.26 ± 0.05) × 10^{-1}		
7-d_3/CH_3I in THF at 0 °C		(2.45 ± 0.06) × 10^{-1}	0.922 ± 0.030
7/CH_3I in DMF at 0 °C	(6.59 ± 0.33) × 10^{-1}		
7-d_3/CH_3I in DMF at 0 °C		(7.24 ± 0.19) × 10^{-1}	0.909 ± 0.051
9/CH_3I in THF at 0 °C	(2.12 ± 0.05) × 10^{-1}		
9-d_5/CH_3I in THF at 0 °C		(2.08 ± 0.07) × 10^{-1}	1.02 ± 0.042

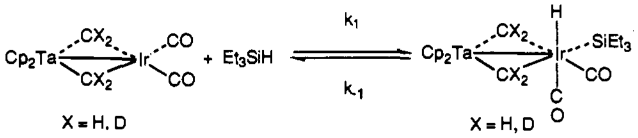
[a] All of the silane rates were calculated assuming that K_{eq} was essentially infinite. [b] Exchange of D into the methylene positions occurs much more slowly than oxidative addition at 0 °C. [c] We neglected to note in the preliminary communication that the value for this entry was measured at 30 °C, rather than at 10 °C. In addition, the present value is an average of four runs each for k_H and k_D.

to the overall KIE. The rate constant for the addition of Et_3SiD to **1** is 3.30 ± 0.18 M^{-1} s^{-1} and to **1-d_4**, 3.77 ± 0.18 M^{-1} s^{-1}. This gives a secondary KIE of 0.875 ± 0.063, in excellent agreement with the values obtained using Et_3SiH. The primary effect calculated from the rates of addition of $Et_3SiH(D)$ to **1** is 1.13, and that calculated from the rates of addition of $Et_3SiH(D)$ to **1-d_4** is also 1.13 ± 0.06. This KIE is normal, but surprisingly small. The consistency of these ratios provides reassurance that we were able to measure the absolute rate constants in each system with good accuracy.

The same four isotope effect determinations were also carried out in THF at 0 °C to look for a solvent effect on the KIE. The second-order rate constant for the addition of Et_3SiH to **1** was 2.79 ± 0.04 M^{-1} s^{-1}, for the addition of Et_3SiH to **1-d_4**, 3.15 ± 0.08 M^{-1} s^{-1}, for the addition of Et_3SiD to **1**, 2.66 ± 0.08 M^{-1} s^{-1}, and for the addition of Et_3SiD to **1-d_4**, 3.05 ± 0.08 M^{-1} s^{-1}. The secondary KIEs which can be derived from these data are 0.886 ± 0.026 (with Et_3SiH) and 0.872 ± 0.035 (with Et_3SiD), with no trend observable from the values derived in toluene. The two primary KIEs, also calculated from these data, are 1.05 ± 0.03 (with **1**) and 1.04 ± 0.04 (with **1-d_4**), consistently lower than the values measured in toluene.

The isotope effect on the reductive elimination reaction of $Et_3SiH(D)$ was derived from the measured values for the kinetic isotope effect on oxidative addition, $k_1^{H/D}$, and the measured and calculated equilibrium isotope effects, $K_{eq}^{H/D}$. For the primary KIE on reductive elimination, $k_{-1}^{H/D}$(primary) = 1.45 ± 0.08, and for the secondary KIE, $k_{-1}^{H/D}$(secondary) = 1.25 ± 0.03 (1.06 per D). Thus, the primary KIE is normal for both oxidative addition and reductive elimination of Et_3SiH (Scheme III), and the secondary KIE is inverse for oxidative addition and normal for reductive elimination of Et_3SiH (Scheme IV).

Scheme IV. Secondary Isotope Effect Results



$K_{H/D}$ = 0.70 (from IR calculation and NMR measurement, assuming $K_{H/D}$(total) = $K_{H/D}$(primary) x $K_{H/D}$(secondary))

$k_{1\ (H/D)}$ = 0.875 (from UV/Vis measurement)

$k_{-1\ (H/D)} = k_1/K_{eq}$ = 1.25

As a test of the effect of a more sterically demanding silane on the secondary KIEs, the rates of oxidative addition of Ph_3SiH to both **1** and **1-d_4** were measured in THF at 10 °C (Scheme II). The equilibrium constant for the reaction of Ph_3SiH to **1** previously measured at this temperature is 5100 M^{-1}, sufficiently high to assume that the oxidative addition proceeds to completion. The rate constant for addition of Ph_3SiH to **1** is 1.32 ± 0.07 M^{-1} s^{-1} and for the addition to **1-d_4** is 1.47 ± 0.10 M^{-1} s^{-1}. From these values a secondary KIE of 0.898 ± 0.077 was calculated, slightly smaller than the KIE for Et_3SiH addition. The isotope effect per deuterium is $(0.898)^{1/4} = 0.973$.

Reactions with Methyl Iodide. The rate of oxidative addition of methyl iodide to both **1** and **1-d_4** was measured in order to test a less sterically demanding substrate (Scheme V) (see Table V for all measured rate constants). In addition, methyl iodide was interesting because its mechanism of oxidative addition is different from that of silanes.[26] The second-order rate constant for MeI addition to **1** in THF at 0 °C was measured to be (1.03 ± 0.02) × 10^{-2} M^{-1} s^{-1} and for the addition to **1-d_4**, (1.37 ± 0.02) × 10^{-2} M^{-1} s^{-1}. A secondary KIE of 0.752 ± 0.018 was derived from these values, larger than any of the KIEs derived from the silane data. The isotope effect per deuterium is $(0.752)^{1/4} = 0.931$.

The oxidative addition of CH_3I was convenient to study over a range of temperatures, both because the reaction went to completion and because rates were in an ideal range ($t_{1/2} \approx$ 60–1000

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[26] 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.

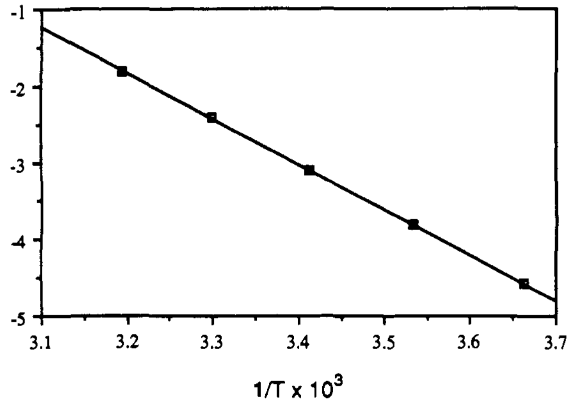


Figure 1. Arrhenius plot for the oxidative addition of MeI to **1** in THF: $\Delta S^{\ddagger} = -26.3$ eu; $\Delta H^{\ddagger} = 11.2 \pm 0.1$ kcal/mol ($r^2 = 1.000$).

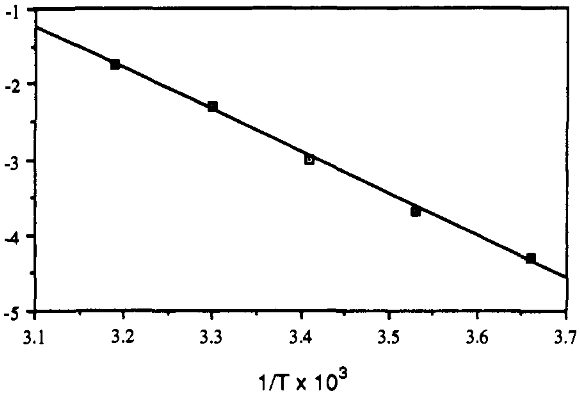


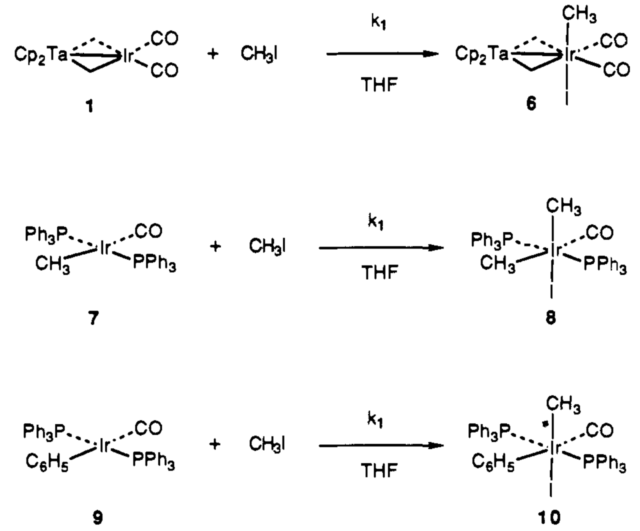
Figure 2. Arrhenius plot for the oxidative addition to MeI to **1-*d*$_4$** in THF: $\Delta S^{\ddagger} = -28.8$ eu; $\Delta H^{\ddagger} = 10.4 \pm 0.3$ kcal/mol ($r^2 = 0.998$).

s) for UV/vis kinetics. The calculated secondary KIEs (from the averaged second-order rate constants in Table V) for this reaction were 0.866 ± 0.038 (0.965 per D) at 10 °C, 0.910 ± 0.038 (0.977 per D) at 20 °C, 0.911 ± 0.033 (0.977 per D) at 30 °C, and 0.937 ± 0.076 (0.984 per D) at 40 °C. The isotope effect decreases with increasing temperature.

A plot of ln k_1 versus $1/T$ was made for both reactions. The best fit line gave an excellent correlation coefficient ($r^2 = 1.000$ for **1** (Figure 1) and $r^2 = 0.998$ for **1-*d*$_4$** (Figure 2)). From the Arrhenius parameters, the enthalpy and entropy of activation were calculated: for the reaction of MeI with **1**, $\Delta H^{\ddagger} = 11.2 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = -26.3 \pm 0.4$ eu; for the reaction of MeI with **1-*d*$_4$**, $\Delta H^{\ddagger} = 10.4 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -28.8 \pm 1.0$ eu. We can use the values of the slope and *y*-intercept of these plots to calculate the difference in activation enthalpies $\Delta\Delta H^{\ddagger}$ (or Arrhenius activation energies E_a) and the ratio of frequency factors A_H/A_D. Because these values are the difference and dividend of two large numbers, the error is significantly larger than in the individual values themselves; we estimate conservatively the frequency factor ratio $A_H/A_D = 3.65 \pm 1.39$ and the Arrhenius activation energy difference $[\Delta E_a]_{H/D} = 0.8 \pm 0.4$ kcal/mol. The iso-isotopic temperature at which both reactions would proceed at the same rate was calculated to be 60 °C. Therefore, above 60 °C the secondary KIE should become "normal". Unfortunately, due to the volatility of CH_3I (bp = 42 °C), these predictions could not be tested.

Reactions in Other Systems. To determine whether secondary β-H/D isotope effects might be general, we extended our study to the secondary KIE for the oxidative addition of MeI to a different iridium center $(CX_3)Ir(CO)(PPh_3)_2$ [X = H, **7**; X = D, **7-*d*$_3$**] (Scheme V). This addition proceeds about 60 times faster than the reaction of MeI with **1** and thus was conveniently measured at 0 °C in THF. The second-order rate constant for the addition of CH_3I to **7** is $(2.26 \pm 0.05) \times 10^{-1}$ M^{-1} s^{-1}, and for addition of **7-*d*$_3$** is $(2.45 \pm 0.06) \times 10^{-1}$ M^{-1} s^{-1}. The secondary KIE calculated from these data is 0.922 ± 0.030, with a value per deuterium of $(0.922)^{1/3} = 0.973$. This is consistent with the values obtained for **1**/**1-*d*$_4$**.

Scheme V



This reaction was also studied in the more polar solvent DMF. The second-order rate constants for the oxidative addition of MeI to **7**, $(6.59 \pm 0.33) \times 10^{-1}$ M^{-1} s^{-1} or to **7-*d*$_3$**, $(7.24 \pm 0.19) \times 10^{-1}$ M^{-1} s^{-1}, are almost three times faster in DMF than in THF at 0 °C. The calculated secondary KIE in DMF is 0.909 ± 0.051 (0.969 per D). This is a bit larger than in THF, but the two values are within 1 standard deviation of each other.

Finally we examined the oxidative addition of CH_3I to the aryl analogue of **7**, $(C_6X_5)Ir(CO)(PPh_3)_2$ [X = H, **9**; D, **9-*d*$_5$**] (Scheme V). The rate constant for the addition of MeI to **9** in THF at 0 °C was $(2.12 \pm 0.05) \times 10^{-1}$ M^{-1} s^{-1} and to **9-*d*$_5$** was $(2.08 \pm 0.07) \times 10^{-1}$ M^{-1} s^{-1}. This gives a secondary KIE for the reaction of 1.02 ± 0.042; i.e., there is no detectable isotope effect.

Attempts to extend these studies to certain other types of reactions were not successful due to inconvenient reaction rates. For example, reaction of bulky phosphines with the TaIr compounds, with both derivatives of Vaska's complex, and with $(COD)Pt(CH(D)_3)_2$ were investigated. In some cases the reaction was too fast to measure with our equipment, and in other cases the ligand did not displace CO. Attempts were also made to measure the rate of oxidative addition of methyl iodide to $(dppe)Pt(CH(D)_3)_2$, but the reaction was not conveniently monitored.

Isotope Effects on Spectroscopic Properties. The effect of isotopic substitution on certain spectroscopic properties of typical organometallic complexes was studied in order to better understand the nature of the secondary KIE. One sensitive technique for detecting small electronic changes at a metal center is to use *trans*-phosphorus-platinum coupling constants as a probe; more electronegative groups have been shown to give higher J_{Pt-P} values.[27] The Pt-P coupling constant for the compound $(dppe)Pt(CH_3)_2$ was measured to be 898.2 Hz, whereas for $(dppe)Pt(CD_3)_2$, J_{Pt-P} was 893.4 Hz. This is consistent with the postulate that deuterium is a better electron donor.

Discussion

Source of the Isotope Effects Observed in the Reactions of 1 and 2. Comparison of the enthalpy and entropy of reaction for the addition of D_2 and H_2 to **2** reveals (as is expected) a slightly stronger Ir-D bond (59.5 ± 0.4 kcal/mol) than Ir-H bond (58.2 ± 0.2 kcal/mol). This is based on the reported bond dissociation energies of H_2 (104.2 kcal/mol) and D_2 (106.0 kcal/mol).[22] Interestingly, the entropy of reaction is more negative for the deuterated system. The explanation for this is not obvious. In any case, the total equilibrium isotope effect (0.54 ± 0.04 at 0 °C) is a combination of a primary effect and secondary effect and at this point it is not possible to separate them.

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In the case of the $Et_3SiH/\mathbf{1}$ and $Et_3SiD/\mathbf{1}\text{-}\boldsymbol{d_4}$ equilibria, the total equilibrium isotope effect is temperature dependent, ranging from 0.53 ± 0.04 at 0 °C to 0.77 ± 0.06 at 60 °C. The isotopic enthalpies and entropies follow the same trend as do the H_2/D_2 oxidative addition: both are more negative for the deuterated system. We presume that $\Delta\Delta H$ is due to the stronger X–D bond, but the $\Delta\Delta S$ again cannot be easily explained.

Because of our inability to measure directly the pure secondary effect in the silane system, the calculated primary (and therefore, secondary) $K_{H/D}$ are only approximations. They do show, however, that the primary effect due to the Si–H bond (which is breaking) and the secondary effect due to the bridging methylenes are roughly equal in magnitude. In addition, both contributions to the total EIE are less than 1. Therefore the KIE on the rate of reductive elimination is larger than the KIE on the rate of oxidative addition. This indicates that the transition state resembles the silane and Ir(I) reactants more than does the Ir(III) oxidative addition products.

Kinetic Isotope Effects in Relation to the EIEs. A point that is immediately apparent upon inspection of the values for the KIE obtained from the oxidative addition of Et_3SiH to **1** is that they are smaller in magnitude than the EIE. This implies that at the transition state the effect exerted by the isotopic substitution is a partially developed interaction which reaches its maximum magnitude in the product. As mentioned in the results section, the temperature dependence of either the primary or the secondary isotope effect could not be measured since the equilibrium constant became too small near 10 °C. However, there is no difference between the KIE at −8 and 0 °C, unlike that seen for reactions of **1** with MeI (see below). This indicates that, in this case, the KIE may arise from enthalpic rather than entropic contributions.

The small solvent effect on the rate is consistent with a concerted cis-addition mechanism of addition of the silane[26] and with a transition state having little charge buildup. Likewise, it is consistent that there is no solvent dependence on the KIE for the reaction. The transition state in both solvents must occur at approximately the same place along the reaction coordinate.

The primary KIEs are normal for both silane addition and elimination as would be expected for an effect caused by bond cleavage. The small size is due either to a small amount of bond-breaking/making in the TS (not very likely), to the presence of a preequilibrium involving an η^1-bound silane, or to a nonlinear TS.[23] Interestingly, the secondary KIE for the oxidative addition is inverse and for the reductive elimination is normal.

Kinetic Isotope Effects for Reactions of Other Substrates with 1. To understand how changes in the steric bulk of a molecule affect the size of the KIE, we examined the oxidative addition of other substrates to **1**. Addition of the bulkier Ph_3SiH (the cone angle for PEt_3 is 132°, whereas for PPh_3 the cone angle is 145°)[28] should produce a larger steric KIE. However, the KIE obtained is 0.898 ± 0.077 (0.973 per D), within error, identical to that seen for Et_3SiH. If anything, this value is smaller than that seen for the smaller substrate. This result is opposite to that expected using the steric argument as the cause of the secondary KIEs.

The use of methyl iodide as a smaller substrate was also investigated because it adds by an S_N2 mechanism.[26] Thus the leaving iodide ion should not interact strongly with the μ-CH_2 groups in the transition state. However, the secondary KIE measured for this reaction at 0 °C (0.752 ± 0.018; 0.931 per D) is larger than that observed for either silane. The trend for these two substrates is apparent: smaller, more nucleophilic substrates exhibit larger KIEs, whereas bulkier substrates show smaller KIEs.

KIEs Observed at Other Metal Centers. Studies of two systems having different metal centers suggest that the effects observed with **1** and **2** are general. The KIEs observed for the reaction of methyl iodide with $CX_3Ir(CO)(PPh_3)_2$ [X = H, **7**; X = D, **7-d_3**] were inverse and of the same order of magnitude (0.971 per D) as for the dinuclear systems. Changing the isotopically substituted group to a phenyl, $C_6X_5Ir(CO)(PPh_3)_2$ [X = H, **9**; X = D, **9-d_5**], resulted in the absence of a detectable KIE, as both protiated and deuterated compounds react at the same rate with methyl iodide in THF at 0 °C. These systems are substituted at the γ- rather than the β-position, and so an attenuation of the KIE is expected.

Table VI. C–H Coupling Constants for the μ-CH_2 Groups of **1** and Its Oxidative Addition Products[a]

compound	J_{CH} (Hz)
$Cp_2Ta(CH_2)_2Ir(CO)_2$	136
$Cp_2Ta(CH_2)_2Ir(CO)_2(CH_3)(I)$	139
$Cp_2Ta(CH_2)_2Ir(CO)_2(H)(SiEt_3)$	136, 139

[a] See ref 67 for details.

Temperature Dependence of the KIE on MeI Addition. For primary effects, temperature dependence studies have focused on hydrogen transfer reactions, and the results related to the structure of the transition state or the presence of tunneling.[29-31] In addition, a few studies on primary KIEs have been done on main-group organometallic compounds.[32,33] Important conclusions about transition states were reached on the basis of the magnitude and the sign of ΔE_a and A_H/A_D. We have been able to locate only one previous study of the temperature dependence of a secondary KIE,[34] which attributes this phenomenon to the formation of several parallel or serial pathways which take different precedence as the reaction conditions change.

Thus it was of interest to perform such a study on one of our systems. The oxidative addition of MeI to **1**/**1-d_4** was conveniently monitored over a broad temperature range. Activation parameters calculated from an Arrhenius plot of these data show that there is a modest contribution from the frequency factor (entropy). The value measured for our secondary effects is $A_H/A_D = 3.65 \pm 1.39$. This appears to be somewhat high, but we feel that the differences between the E_a and A values are too small, and the errors in them too large, to reliably determine whether the KIE arises primarily from an enthalpic or entropic effect.

Cause of Secondary Isotope Effects in Oxidative Addition Reactions. We consider here how the four possible explanations summarized above might account for the secondary β-deuterium isotope effects reported in this paper.

(1) Hyperconjugation. One potential source of the observed isotope effects might be hyperconjugation of the CH_2 group and the empty 6p orbital at iridium (all other orbitals with the correct symmetry are either filled or too high in energy). A related, but not identical, source of a KIE might be an agostic interaction between the μ-CH_2 group and the iridium. These ground-state interactions would be lost upon oxidative addition of the substrate. This may be considered the inverse of the effect typically seen in organic carbocation reactions. Hydrogen, because it has a higher zero point energy than deuterium, is better able to hyperconjugate with the iridium center. There are, however, four complications associated with such a proposal that tend to limit the extent to which hyperconjugation could contribute to the isotope effects: (a) the 6p orbital is very high in energy relative to the C–H bond, minimizing overlap; (b) the angle between the two orbitals is approximately 45°, also minimizing overlap; (c) a typical C–C bond length is 1.5 Å,[35] and the Ir–C bond in $Cp(Ind)Ta(CH_2)_2Ir(CO)_2$ is 2.2 Å, again reducing overlap; and (d) for reactions in poorly overlapping constrained systems, such as cyclobutyl tosylate solvolyses, hyperconjugation is reported to be nearly negligible.[36] From these arguments, we suggest that contributions from this interaction to the rate of oxidative addition/reductive elimination would at best be minimal.

However, even assuming a small hyperconjugative contribution, the highest occupied molecular orbital (the one that interacts most

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(36) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill Co.: New York, 1962.

Table VII. ν(CO) for Oxidative Addition Products of $Cp_2Ta(CH_2)_2Ir(CO)_2$ in THF

compound	ν(CO) (cm^{-1})
$Cp_2Ta(CH_2)_2Ir(CO)_2$	1946, 2008
$Cp_2Ta(CH_2)_2Ir(CO)_2(Me)(I)$	2023, 2067
$Cp_2Ta(CH_2)_2Ir(CO)_2(SiEt_3)(H)$	1958, 2025
$Cp_2Ta(CH_2)_2Ir(CO)_2(SiPh_3)(H)$	1973, 2035

strongly with the substrate, i.e., MeI or Et_3SiH) is not the 6p but the $5d_{z^2}$ orbital. Because it is occupied, this orbital cannot hyperconjugate with the C–H bond of the bridging methylenes.

(2) Hybridization Changes. Because our measured equilibrium isotope effects were larger than the kinetic effects, we considered the possibility that a change in hybridization at the bridging methylenes might be occurring. To check on this, we measured the methylene ^{13}C–H coupling constants. As can be seen from Table VI, the coupling constants are consistently slightly larger for the Ir(III) complexes than for the analogous Ir(I) complexes. The intermediate values present at the transition state must differ from those of the starting materials by a very small amount. (We suggest that this small change in J_{CH} is due to the higher electronegativity of the Ir(III) center compared to the Ir(I) center.[37])

(3) Steric Differences. The remaining two hypotheses (that the isotope effect is due to either steric or inductive differences between the methylene C–H and C–D bonds) are much harder to differentiate. Both effects would predict an inverse KIE for oxidative addition (steric: D is smaller; inductive: D is a better electron donor) and a normal effect for reductive elimination. For reactions that might be used to distinguish the two mechanisms, such as addition of phosphine to the Ir center, either the reactions were too fast to monitor or exchange processes occurred in conjunction with addition processes that made interpretation of the experiments impossible.

However, several lines of evidence argue against the steric effect postulate. First, and most importantly, the use of sterically different substrates does not produce predictably different ΔKIEs. For example, Ph_3SiH (based only on steric arguments) should result in a larger KIE than should Et_3SiH. This is not observed. The use of the much smaller substrate MeI, based solely on steric arguments, would also result in a smaller KIE relative to Et_3SiH; again, the opposite trend is observed.

A further concern about the steric argument is that most theoretical and experimental papers assume the steric effect is due almost solely to enthalpic and not entropic considerations.[38,39] This is clearly not the case for the reaction of MeI with **1/1-d_4**: $\Delta\Delta S^\ddagger$ contributes, at room temperature, twice as much to the KIE as does $\Delta\Delta H^\ddagger$.

(4) Inductive Differences. On the other hand, a reasonable body of evidence points to the influence of the better electron-donating power of deuterium on the rate of the reactions observed in these systems. In the oxidative additions to **1/1-d_4**, the KIE is largest when using MeI; this reaction also has the most charge development in the rate-determining transition state.[40] Second, the KIE seems sensitive to the type of carbon that is bound to iridium; i.e., the KIE per D for allyl-like **1** is larger than the KIE per D for alkyl-substituted **7**. Third, iridium goes from a formal oxidation state of +1 in the starting materials to a formal oxidation state of +3 in the products. As shown by ν(CO) for the derivatives of **1** listed in Table VII, the iridium is more electron-poor in the products (the CO absorptions appear at higher frequencies). We therefore feel that the better electron-donating ability of D relative to H provides the most reasonable explanation for our results at the present time.

Experimental Section

General. All heterodinuclear compounds reported here have been previously synthesized and fully characterized.[20,23,41] Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere in a Vacuum Atmospheres 553-2 drybox equipped with an M6-40-1 Dri-train or using standard Schlenk techniques.

All ^1H and ^{31}P NMR spectra were recorded on 300-MHz instruments at the University of California, Berkeley NMR facility. The 300-MHz instrument was constructed by Mr. Rudi Nunlist and interfaced with a Nicolet 1280 computer. Infrared spectra were recorded on a Perkin-Elmer Model 1550 Fourier transform spectrophotometer, and the bands are reported in cm^{-1}. Ultraviolet–visible spectra were recorded on a Hewlett-Packard Model 8450 UV/vis spectrophotometer. Samples were prepared in the drybox and spectra recorded with the use of a quartz cuvette fused to a Kontes vacuum stopcock.

Toluene and THF were distilled from sodium/benzophenone. Dimethylformamide and triethylsilane were distilled from activated 4-Å molecular sieves. Methyl iodide was distilled from $CaCl_2$ and stored over a copper wire. Et_3SiD was synthesized from Et_3SiCl and $LiAlD_4$.[42] Unless otherwise noted, all other reagents were used as received from commercial suppliers.

$Cp_2Ta(CH_2)_2Ir(CO)_2$ and $Cp_2Ta(CD_2)_2Ir(CO)_2$,[41] (bis(diphenylphosphino)ethane)$Pt(CH_3)_2$ and (bis(diphenylphosphino)ethane)$Pt(CD_3)_2$,[43] $(PPh_3)_2Ir(CO)CH_3$ and $(PPh_3)_2Ir(CO)CD_3$,[44] $(PPh_3)_2Ir(CO)C_6H_5$ and $(PPh_3)_2Ir(CO)C_6D_5$[45] were all synthesized via published procedures or their modifications.

Reactions with gases (other than H_2 or D_2) or transferrable liquids involved condensation of a calculated pressure (ideal gas law) of gas from a bulb of known volume into the reaction vessel at 77 K. Because H_2 and D_2 are gases at this temperature, these were added directly into the reaction vessel held at 77 K and, in the case of NMR tubes, flame sealed 1 cm above the level of the liquid nitrogen (integration of the hydrogen peak vs an internal standard in the ^1H NMR spectrum verified that the desired amount had been added).[46] Sealed NMR tubes were prepared by connecting the tube to a Kontes vacuum adaptor via a Cajon joint,[47] freezing and degassing the sample once (unless otherwise stated), and flame sealing the tube with an oxygen/propane torch. Unless noted otherwise, all reactions were carried out at ambient temperature.

Thermodynamic Measurements and Calculations: General. A weighed amount of the metal complex was dissolved in approximately 0.45 mL of the NMR solvent, and the resulting solution was added to a Wilmad PS-505 NMR tube. The tube was set up as described above for the case of H_2 or D_2. Et_3SiH or Et_3SiD were also added to the NMR tube by vacuum transfer, waiting at least 10 min for the transfer because the silanes tend to condense slowly. All tubes were flame sealed, thawed, and then allowed to stand at room temperature for 3 h in order to reach equilibrium (the hydrogen reactions were also periodically shaken by hand). The solution volume was calculated based upon the standard 74.5 mm of solvent = 1 mL (1 mL of acetone was added to four Wilmad PS-505 NMR tubes via a syringe, and the height of the solvent was found to be 74.5 ± 0.2 mm). The reactions were monitored on a 300-MHz NMR spectrometer with a calibrated thermocouple placed in the probe. The samples were equilibrated at each temperature for 10 min before taking the spectrum. Spectra were taken sequentially as the probe was heated to the maximum temperature and then again as the probe was cooled to the minimum temperature, and thus two points were obtained for each temperature (the K_{eq} values agreed to within 5%). Concentrations of the molecules were measured against ferrocene as the internal standard, and K_{eq} was calculated using standard equations. Plots of ln K_{eq} vs $1/T$ were made using the Igor graphing program,[48] and the reported standard deviations were obtained from the best fit of the line to the points.

Kinetics: General. Standard solutions were prepared in the drybox in volumetric flasks and stored in the drybox freezer at −30 °C. Individual runs were prepared in the drybox by transferring aliquots of

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(48) The Igor graphing and data analysis software are distributed by WaveMetrics of Lake Oswego, OR.

standard solutions with a graduated pipet into a quartz cuvette fused to a Kontes vacuum adapter equipped with a stir bar, a 14/20 rubber septum (for the ground glass joint), and a 24/40 rubber septum (to fit over the top of the screw joint; the Kontes Teflon-brand stopcock was not used). The sample was taken out of the drybox and placed into a Hewlett-Packard temperature-controlled cell holder[49] equipped with a magnetic stirrer and a nitrogen gas inlet (to prevent condensation of water during a kinetic run). UV/vis spectra were taken once a minute until the peak intensities were stable, at which point the solution was assumed to be thermally equilibrated. The reactant (kept in a vial under N_2) was added via a 10-μL syringe and the preprogrammed kinetics run was initiated. Spectra were taken, in general, three times every half-life for 7 half-lives. If possible, reactions, were followed at one wavelength in the visible region and one wavelength in the UV region.

Plots of A (related to c/c_0 by Beer's law) or ln $(A_\infty/(A - A_\infty))$ (for decreasing absorbances) or ln $(A_\infty/(A_\infty - A))$ (for increasing absorbances) (A = measured absorbance intensity, A_∞ = infinity value of absorbance intensity, c = concentration at time t, c_0 = initial concentration) vs time were plotted using the Igor graphing program.[50] Both the nonlinear fit and the linear fit of the data produced identical pseudo-first-order rate constants (within 1 standard deviation); the values reported are those obtained from the linear fits. Second-order rate constants were calculated by standard kinetic equations.[51]

Because the silane oxidative addition reactions did not go to completion but approached an equilibrium, the slope (k_{obs}) of the ln $(A_\infty/(A - A_\infty))$ vs t plots for the reaction was equal to $k_1[R_3SiX] + k_{-1}$. From the measured values of K_{eq} and k_{obs}, the second-order rate constant for oxidative addition (k_1) and the first-order rate constant for reductive elimination (k_{-1}) could be calculated. However, in mixed systems, such as $Cp_2Ta(CH_2)_2Ir(CO)_2/Et_3SiD$, proton–deuterium exchange prevented us from measuring an accurate K_{eq}. Thus, the rate constants for the mixed systems were measured at low temperatures where K_{eq} was very large ($\sim 5 \times 10^3$), and k_1 and k_{-1} were calculated assuming the reaction went to completion.[52]

Activation parameters for the oxidative addition of MeI to **1** and **1-*d*$_4$** were obtained by plotting ln k_1 (the second-order rate constant, often the average value for several runs) versus $1/T$ to give a typical Arrhenius plot. From the values of the slope and y-intercept the enthalpy and entropy of activation were calculated using standard equations.

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Supplementary Material Available: Table of reaction parameters for setting up the thermodynamics studies, table of reaction parameters for setting up the kinetic studies, and two tables listing all of the measured rate constants (7 pages). This material is provided with the archival edition of the journal, which is available in many libraries. Alternatively, ordering information is given on any current masthead page.

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(49) Calibrated by Mr. Robert Minto and found to be accurate within the reported temperature range.

(50) The Igor graphing program was modified by Dr. Kevin Kyle to calculate the infinity point and rate constant for a first-order reaction.

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(52) This introduced $\sim$2% error in the absolute values of k_1 and k_{-1}, but did not affect the KIE since the magnitude and direction of the error were nearly identical for both isotopes.