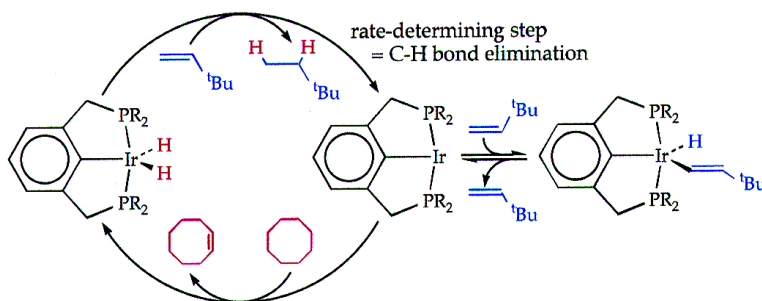


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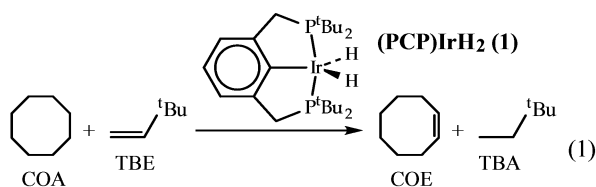
Mechanism of Alkane Transfer-Dehydrogenation Catalyzed by a Pincer-Ligated Iridium Complex

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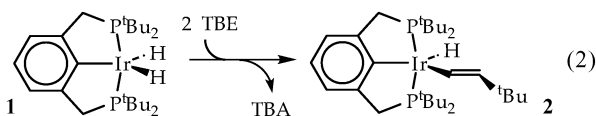
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The selective dehydrogenation of alkanes and alkyl groups is a reaction with a wide range of applications of great potential value.¹ Presently, the most effective systems for selective alkyl-group dehydrogenation are those based upon pincer-ligated iridium.^{2,3} Herein we report elucidation of the reaction mechanism of the first and prototypical example of such reactions: transfer-dehydrogenation of cyclooctane/*tert*-butylethene (COA/TBE) catalyzed by (PCP)IrH₂ (**1**; PCP = 2,6-C₆H₃(CH₂P^tBu₂)₂), to give cyclooctene (COE) and 2,2-dimethylbutane (*tert*-butylethane; TBA).

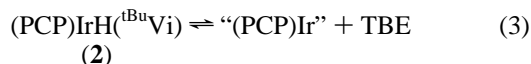


Our approach to the mechanism involves independent determination of the kinetics of both the catalytic system and its stoichiometric component reactions.

In the absence of alkane (in mesitylene solvent), **1** reacts with TBE: 1 equiv of TBE is hydrogenated, and a second equivalent undergoes vinylic C–H addition to (PCP)Ir (eq 2) to give (PCP)IrH(^tBuVi) (**2**; ^tBuVi = *trans*-2-[*tert*-butyl]vinyl).⁴

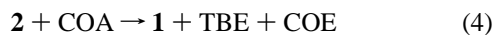


We have previously reported **2** and found that it undergoes rapid exchange with free TBE (on the NMR time scale) at ambient temperature via reversible loss of TBE (eq 3).⁴



The kinetics of reaction 2 were studied by monitoring the disappearance of **1** and appearance of **2** at 55 °C in mesitylene. The reaction was found to proceed with a rate constant $k_h = 0.57 \text{ M}^{-1} \text{ min}^{-1}$, where $-d[\mathbf{1}]/dt = d[\mathbf{2}]/dt = k_h[\mathbf{1}][\text{TBE}]$.

When COA is added to **2** (in *p*-xylene solvent at 55 °C), a rapid reaction ensues (eq 4).

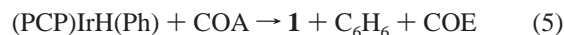


The sum of reactions 2 and 4 is the catalytic reaction of eq 1. Thus, the two reactions constitute a possible mechanism for the catalytic transfer-dehydrogenation.

Unfortunately, whereas it was possible to isolate the suspected half of the catalytic cycle leading to TBE hydrogenation (eq 2)

and then study its kinetics, the suspected second half of the cycle (eq 4) is too rapid to measure at 55 °C at low [TBE] (<ca. 0.2 M). Higher [TBE] inhibited reaction 4, but under such conditions reaction 2 then proceeds too rapidly to allow the independent measurement of the rate of reaction 4. Nevertheless, the observation of inhibition by added TBE suggests that the reaction proceeds via free “(PCP)Ir”.

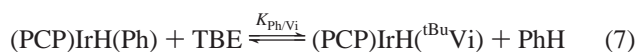
We therefore used an alternative source of “(PCP)Ir” which permitted study of COA dehydrogenation (as in eq 4) without the complications introduced by the presence of free TBE. (PCP)IrH(Ph) undergoes dissociative hydrocarbon exchange in analogy with the behavior of **2** (eq 3). Accordingly, it reacts with COA (eq 5), in analogy with the reaction of **2** (eq 4).



The kinetics of eq 5 (55 °C, *p*-xylene solvent) are found to be consistent with the rate law of eq 6, with $k_{\text{dh}(\text{IrPh})} = 0.0023 \text{ min}^{-1}$.

$$-d[(\text{PCP)IrH(Ph)}]/dt = d[\mathbf{1}]/dt = k_{\text{dh}(\text{IrPh})}[(\text{PCP)IrH(Ph)}][\text{COA}][\text{C}_6\text{H}_6]^{-1} \quad (6)$$

To extrapolate the analogous rate constant for the actual complex of interest, **2**, it is sufficient to determine the equilibrium constant for eq 7;⁵ $K_{\text{Ph/Vi}}$ was found to equal 0.33.



Applying this value to $k_{\text{dh}(\text{IrPh})}$, we obtain a value of 0.0070 min^{-1} for k_{dh} , the analogous rate constant for the reaction of **2** with COA (eq 4). This extrapolation is valid assuming that reactions 4 and 5 both proceed through a pre-equilibrium involving (PCP)Ir or through *any* other common intermediate.

Based on the mechanism of eqs 2 and 4 and the corresponding rate laws, the ratio of [**2**] to [**1**] under catalytic conditions can be predicted to be that of eq 8.⁵

$$[\mathbf{2}]/[\mathbf{1}] = k_h[\text{TBE}]^2/k_{\text{dh}}[\text{COA}] \quad (8)$$

The catalytic reaction (eq 1) was monitored in situ (³¹P and ¹H NMR) at 55 °C. A plot of [**2**]/[**1**] vs [TBE]² ([TBE] = 0.12–0.72 M) yields a straight line, in excellent agreement with eq 8.⁵ The slope, $k_h/k_{\text{dh}}[\text{COA}]$, yields $k_h/k_{\text{dh}} = 56 \text{ M}^{-1}$.

The catalytic turnover rate predicted by the mechanism of eqs 2 and 4 is expressed in the overall rate law of eq 9.⁵

$$d[\text{COE}]/dt = k_h k_{\text{dh}} [\text{TBE}] [\text{COA}] [\text{Ir}_{\text{tot}}] / (k_{\text{dh}} [\text{COA}] + k_h [\text{TBE}]^2) \quad (9)$$

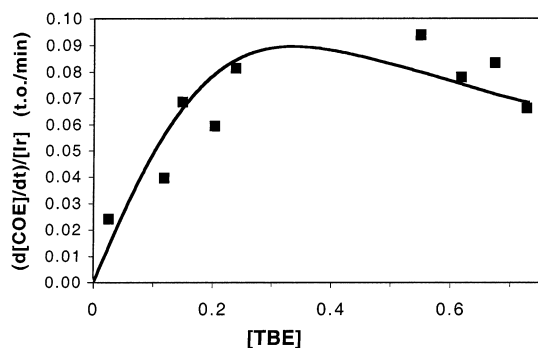


Figure 1. Rate of transfer-dehydrogenation (eq 1) vs [TBE].

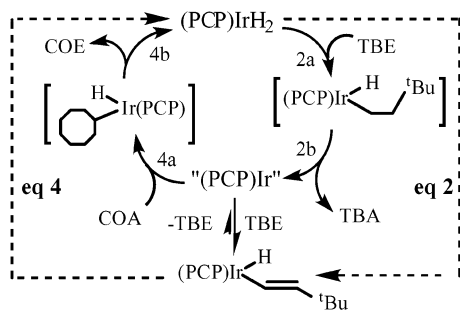


Figure 2. Mechanism of eq 1 (presumed intermediates in brackets). Outer (dashed) arrows refer to eqs 2 and 4 (overall observed reactions, with rate constants k_h and k_{dh}). 2a, 2b, 4a, 4b are inferred reaction steps.

According to eq 9, in the limit of low [TBE], the catalytic rate is equal to $k_h[\text{TBE}][\text{Ir}_{\text{tot}}]$ (first order in [TBE]), while in the limit of high [TBE], the rate should be $k_{dh}[\text{TBE}]^{-1}[\text{COA}][\text{Ir}_{\text{tot}}]$ (inverse first-order in [TBE]). Accordingly, the curve of rate vs [TBE] reveals a maximum (at ca. 0.34 M TBE; Figure 1).

The curve shown in Figure 1 is calculated according to eq 9 to a best fit of the data, with k_h/k_{dh} held fixed at 56 M^{-1} (the value obtained from eq 8 and a plot of $[2]/[1]$ vs $[\text{TBE}]^2$). This therefore represents a one-parameter fit yielding the two rate constants, each obtained solely from in situ observation of the catalytic system: $k_h = 0.53 \text{ M}^{-1} \text{ min}^{-1}$, $k_{dh} = 0.0094 \text{ min}^{-1}$.

We now arrive at the critical question in the assessment of the proposed mechanism of eqs 2 and 4: Are the rate constants obtained from the stoichiometric experiments consistent with those obtained independently from the catalytic experiments? Considering experimental error and possible effects of different solvents (stoichiometric runs were necessarily conducted in non-alkane solvents), the agreement between the sets of rate constants is excellent (catalytic $k_h = 0.53 \text{ M}^{-1} \text{ min}^{-1}$, $k_{dh} = 0.0094 \text{ min}^{-1}$; stoichiometric $k_h = 0.57 \text{ M}^{-1} \text{ min}^{-1}$, $k_{dh} = 0.0070 \text{ min}^{-1}$). The overall set of kinetic equations is thus strongly overdetermined, and we consider these kinetics to be, effectively, proof of the mechanism of eqs 2 and 4 (Figure 2).

Somewhat surprisingly, under typical conditions ([TBE] < ca. 0.3 M), the TBE-hydrogenation part of the cycle is rate-determining. To determine the rate-determining reaction step (within the overall reaction 2), a labeling experiment was designed to reveal if insertion of TBE into the Ir–H bond is irreversible (i.e., if $k_{2b} \gg k_{-2a}$, Figure 3). (PCP)IrD₂ was reacted with TBE. The initial rate of formation of the H/D-exchanged product, CH₂=CD'Bu, was found to be 4.8 times greater than that of the hydrogenated product, CH₂D–CHD–(tBu). Neglecting isotope effects,⁵ we therefore obtain $k_{-2a}/k_{2b} = 9.6$. (Statistically, formation of CH₂=CD'Bu reflects half the rate of β -H/D elimination).

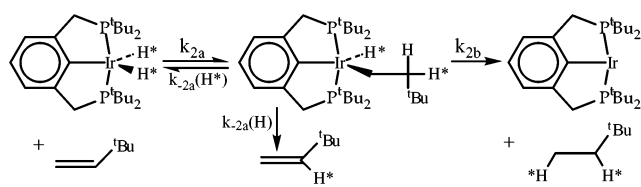


Figure 3. Reaction of **1** with TBE: competition between β -H (or β -D) elimination and C–H bond elimination ($\text{H}^* = \text{H}$ or D).

The labeling experiment of Figure 3 demonstrates that the rate-determining step of reaction 2, and thus the rate-determining step of the catalytic cycle under typical conditions, is C–H elimination of TBA (2b, Figure 2). Based on considerations of microscopic reversibility, C–H addition must be the rate-determining step of the reverse reaction, the (hypothetical) *dehydrogenation* of TBA. This conclusion can be further extrapolated to the terminal dehydrogenation of *n*-alkanes (the lack of a bulky *t*-Bu group should facilitate β -H elimination more than C–H addition) and probably to cycloalkanes. This finding is an important contrast with previously reported alkane dehydrogenation systems, in which β -H elimination was found to be rate-determining;¹ it is clearly relevant, for example, to the high regioselectivity shown by **1** in the terminal dehydrogenation of *n*-alkanes.³

In summary, the mechanism of (PCP)Ir-catalyzed COA/TBE transfer-dehydrogenation has been elucidated. The two segments of the cycle have been observed independently, and the nature of the rate-determining step within each segment has been determined. Noteworthy features of the mechanism include the following:

- Although olefin hydrogenation is one of the most widely and readily catalyzed reactions of organometallic complexes, the rate-determining (slow) segment of the present cycle under typical conditions is hydrogenation of TBE.
- Although C–H addition is often assumed to be the “difficult” step in alkane functionalization, in this case C–H *elimination* of hydrogenated alkane product (TBA; eq 2b) is apparently rate-determining.
- In the regime where dehydrogenation is the rate-determining segment (very high [TBE]), C–H addition is inferred to be rate-determining. Nevertheless, a substantial contribution to the overall barrier derives from the thermodynamic cost of eliminating the vinyl C–H bond of TBE prior to addition of the alkane C–H bond.

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Supporting Information Available: General experimental information, derivations of eqs 8 and 9, graphical results and discussion concerning eqs 5 and 8, discussion of isotope effects, and kinetics-modeling procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Previous reports of (PCP)Ir-catalyzed transfer-dehydrogenation (ref 2) involved temperatures ≥ 150 °C; however, for the purposes of mechanistic study, 55 °C was found to give much more convenient rates.
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- See Supporting Information.

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