# **ORGANOMETALLICS**

# Scope and Mechanism of Homogeneous Tantalum/Iridium Tandem Catalytic Alkane/Alkene Upgrading using Sacrificial Hydrogen Acceptors

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**Supporting Information** 

**ABSTRACT:** An in-depth investigation of a dual homogeneous catalyst system for the coupling of alkanes and alkenes based on an early-/late-transition-metal pairing is reported. The system is composed of Cp\*TaCl<sub>2</sub>(alkene) for alkene dimerization and pincer-iridium hydrides for alkane/alkene transfer hydrogenation. Because there is no kinetically relevant interaction between the two catalysts, the tandem mechanism can be entirely described using the two independent catalytic cycles. The alkene dimerization mechanism is characterized by an entropically disfavored pre-equilibrium between Cp\*TaCl<sub>2</sub>(1-hexene) + 1-hexene and



 $Cp^*TaCl_2$ (metallacyclopentane) ( $\Delta H^\circ = -22(2)$  kcal/mol;  $\Delta S^\circ = -16(2)$  eu); thus, the overall rate of alkene dimerization is positive order in 1-hexene (exhibiting saturation kinetics), and increases only modestly with temperature. In contrast, the rate of 1-hexene/*n*-heptane transfer hydrogenation catalyzed by *t*-Bu[PCP]IrH<sub>4</sub> is inverse order in 1-hexene and increases substantially with temperature. Styrene has been investigated as an alternate sacrificial hydrogen acceptor. Styrene dimerization catalyzed by Cp\*TaCl<sub>2</sub>(alkene) is considerably slower than 1-hexene dimerization. The conversion of styrene/heptane mixtures by the Ta/Ir tandem system leads to three product types: styrene dimers, coupling of styrene and heptane, and heptene dimers (from heptane). Through careful control of reaction conditions, the production of heptene dimers can be favored, with up to 58% overall yield of heptane-derived products and cooperative TONs of up to 12 and 10 for Ta and Ir catalysts, respectively. There is only slight inhibition of Ir-catalyzed styrene/*n*-heptane transfer hydrogenation under the tandem catalysis conditions.

# INTRODUCTION

As exploitation of traditional crude oil reserves becomes economically and geopolitically more volatile, and concern regarding CO<sub>2</sub> emissions from the current inefficient use of carbon-based energy carriers increases, many countries and industries are actively pursuing alternate fuel sources for the global transportation fleet.<sup>1</sup> These factors are driving the development of new technologies for fuel production from carbon sources such as bitumen and kerogen (so-called oilsands and shale oil),<sup>2</sup> natural gas,<sup>3</sup> and biomass.<sup>4</sup> In contrast to fuels derived from crude oil that are predominantly collected by fractional distillation, obtaining hydrocarbons in the desired weight range from these alternate carbon sources often requires extensive refining and synthetic manipulation, such as catalytic cracking<sup>5</sup> and Fischer-Tropsch synthesis.<sup>6</sup> In addition to the optimal fuel-range hydrocarbons  $(C_8-C_{22})$ , lighter alkanes and alkenes are abundant products of these processes. Currently, light hydrocarbons  $(C_{<6})$  have little value as fuels due to their volatility (liquids) and low volumetric energy density (gases). This inherent inefficiency in fuel production will increase both the economic and environmental cost of our continued exploitation of these emerging carbon sources.

In order to better utilize low-carbon-number energy carriers, these feedstocks need to be upgraded to higher molecular weight compounds, ideally in the diesel fuel range  $(C_{10}-C_{22})$ .

Such a process must necessarily perform chemistry on alkanes under relatively mild conditions: the entropic cost of coupling smaller carbon chains into larger ones means that high temperatures are thermodynamically incompatible. One possible technology for achieving this goal, alkane metathesis, is currently under investigation by a number of research groups.<sup>7</sup> Alkane metathesis operates via combined alkane dehydrogenation and alkene metathesis using either two separate catalysts or one catalyst capable of both transformations. In the ideal case, two  $C_n$  alkanes afford one  $C_{2n-2}$  alkane and one equivalent of ethane in an approximately thermoneutral reaction; however, alkane metathesis tends toward a statistical carbon number distribution of alkanes, with few examples that can achieve any selectivity for the desired  $C_{2n-2}$  product.<sup>8</sup> While further catalyst development efforts may result in a viable process, alternative methods for upgrading light hydrocarbons are also needed.

Recently, we outlined a complementary approach toward light hydrocarbon upgrading based on a tandem<sup>9</sup> alkane dehydrogenation—alkene dimerization sequence.<sup>10</sup> Rather than using alkanes as the sole reactant, this process takes advantage of the mixed nature of many light byproduct streams by

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Scheme 1. Tandem Catalytic Alkene Dimerization/Transfer Hydrogenation Approaches toward Hydrocarbon Upgrading



incorporating both alkanes and alkenes as substrates. In an asyet unrealized ideal system (Scheme 1, left), one catalyst dimerizes the 1-alkene component of the mixed gas or liquid feedstock. Transfer hydrogenation by a second catalyst converts the alkane component to a 1-alkene, with concomitant hydrogenation of the  $C_{2n}$  alkene to the desired  $C_{2n}$  alkane product. The 1-alkene thus formed is then coupled with another one equivalent of 1-alkene by the dimerization catalyst, continuing the synthetic cycle. Overall, this process couples an alkane and alkene to a higher alkane, with no byproducts generated. This net alkene hydroalkylation parallels alkane/ alkene coupling reactions using strong acids,<sup>11</sup> though using an entirely different mechanistic approach. While acid-catalyzed alkylations rely on carbocation intermediates, which give highly branched products, the tandem catalytic process in Scheme 1 could be tailored to give mostly linear products by a careful choice of dimerization catalyst.<sup>1</sup>

In our initial communication,<sup>10</sup> we reported a dual homogeneous catalytic system for alkane/alkene coupling based on an early-/late-transition-metal combination: alkene dimerization is effected by Cp\*TaCl<sub>2</sub>(alkene) catalyst 1 (Cp\* =  $C_5Me_5$ ),<sup>13</sup> while transfer hydrogenation is performed by pincerligated iridium catalyst 2 (Figure 1).<sup>14–17</sup> This system is able to



Figure 1. Ta and Ir precatalysts investigated for tandem catalytic alkane/alkene coupling.

couple 1-hexene and *n*-heptane with a high degree of catalyst cooperativity; however, the full synthetic cycle shown on the left of Scheme 1 has not been achieved. Instead, this system operates by a sacrificial  $H_2$  acceptor pathway, in which the alkene substrate, and not the  $C_{2n}$  product, acts as the hydrogen acceptor (Scheme 1, right). Thus, for every one equivalent of alkane upgraded, one equivalent of a different alkane is generated. This sacrificial acceptor reactivity leads to both dehydrogenative alkane/alkene coupling (Scheme 1, right top) and double-dehydrogenative alkane coupling (hereafter referred to as "alkane coupling", Scheme 1, right bottom) when R and R' are different.

In order to elucidate the features of this tandem catalytic process, we have studied the mechanism of 1-hexene/n-heptane coupling in considerable detail. These results indicate that the two catalysts operate with opposing kinetic features, meaning the ideal reaction conditions (i.e., substrate concentration and temperature) for each process are very different. Thus, the optimal set of conditions for tandem catalysis is a compromise between the two extremes. Furthermore, in an effort to identify other alkene/alkane combinations that are amenable to tandem catalysis, we have used styrene as a sacrificial hydrogen acceptor. By adjusting the ratio of the two catalysis, a high degree of selectivity (>26:1) for tandem catalysis in this styrene/alkane system can be realized.

# RESULTS AND DISCUSSION

**Mechanistic Studies of 1-Hexene Dimerization.** One of the most significant findings during our initial tandem catalysis investigations<sup>10</sup> is that the tantalum and iridium catalysts operate independently in solution. This has been established by demonstrating that the initial rates of alkene dimerization and alkene/alkane transfer hydrogenation are the same in tandem and individual reactions (Figure 2). Thus, a complete picture of the tandem system can be constructed by overlaying the mechanisms of the two individual processes.

Both the tantalum system  $1^{13}$  and iridium system  $2^{14-17}$  have been well studied by other research groups; however, we required a detailed understanding of the specific mechanistic features of each catalyst under the conditions used for the tandem reactions. Therefore, we have conducted an in-depth kinetic study of the dimerization of 1-hexene catalyzed by 1 at elevated temperatures and over a wide range of initial substrate concentrations. This study complements previous kinetic work by the Schrock group carried out at lower temperatures (0–90 °C).<sup>13d</sup> They found that increasing [1-octene] (1.4–6.4 M) leads to a very small increase (1.3×) in the initial rate of dimerization at 50 °C, consistent with Cp\*TaCl<sub>2</sub>-(metallacyclopentane) as the major resting state.

One detail in the original synthetic work by Schrock et al. that caught our attention concerns the temperature stability of putative catalytic intermediates: specifically, that Cp\*Ta-Cl<sub>2</sub>(alkene) complexes undergo rapid decomposition at 100 °C *in the absence of added alkene*.<sup>13c</sup> This fact led the authors to speculate that catalyst decomposition at these elevated temperatures should be especially problematic at low concentrations of 1-alkene, since these conditions would favor Cp\*TaCl<sub>2</sub>(alkene) as the catalyst resting state (vide



**Figure 2.** Time evolution plot of the tandem catalytic coupling of 1-hexene/*n*-heptane: (top) reaction conditions and products observed; (bottom left) time course plot for concentrations of all observed species; (bottom right) expansion and simplification showing formation of  $C_{12}$  (from 1-hexene dimerization) and *n*-hexane (from 1-hexene/*n*-heptane transfer hydrogenation). Colored points are from tandem reactions (same data as chart on left), while black hollow points represent several individual catalytic runs with either 1 (diamonds) or 2 (squares). These data indicate that the rates of the individual catalytic reactions are identical with the rates observed during tandem catalysis, and therefore the two catalysts operate independently.

infra). It is surprising, then, that our tandem catalytic alkane/ alkene coupling operates under exactly this set of conditions with no apparent catalyst decomposition, even over >30 h with 1-alkene added slowly via syringe pump. Thus, we sought to identify the catalyst resting state under conditions relevant to tandem catalysis.

The dimerization of  $\sim$ 240 mM 1-hexene catalyzed by 1 at 100 °C results in the formation of several products (eq 1). Two



 $C_{12}$  regioisomers are observed (~3:1 ratio), as well as a small amount of *cis*- and *trans*-2-hexene (~6% combined yield). No 3-hexenes are observed. Monitoring this dimerization reaction over time by GC/FID gives the profile shown in Figure 3. There is clearly a rate dependence on the concentration of 1-hexene (i.e., the reaction is not zero order in [1-hexene]). Additionally, the regioisomer ratio remains relatively constant, though there is a small change over time (3.5:1 at 20% conversion, 3.2:1 at 99% conversion).

Attempts to fit the consumption of 1-hexene or the production of either regioisomer to simple exponential functions result in poor correlation. This indicates that a more complex rate law is operative during the course of the reaction. An examination of the proposed catalytic cycles (Scheme 2), and the application of several reasonable



Figure 3. Time evolution plot of the dimerization of 1-hexene (240 mM) catalyzed by 1 (8 mM) at 100  $^\circ$ C (three runs).

assumptions allowed Schrock et al. to derive rate laws for the formation of both regioisomers (eqs 2 and 6). $^{13d}$ 

These dimerization reactions are proposed to proceed through reversible oxidative coupling of two 1-alkenes at a Ta(III) center (A to B or B') followed by irreversible decomposition of the tantalacyclopentanes B or B' through a remarkable ring-contraction mechanism elucidated previously<sup>13b,d</sup> (not shown). Finally, displacement of the product  $C_{2n}$ alkene in C/C' by the 1-alkene substrate regenerates the Ta(III) complex A. Recall that it is species A that is thermally unstable and thus apparently unsuitable as a catalyst resting state at elevated temperatures. It is therefore important to determine the values of  $K_{eq}$  and  $K_{eq}'$  under tandem catalysis reaction conditions, which will reveal which side of the A + 1alkene  $\leftrightarrows B$  equilibrium is favored and thus the predominant tantalum resting state. Scheme 2. Proposed Catalytic Cycles for the Dimerization of 1-Alkenes into Two Regioisomers Catalyzed by  $1^a$ 



In order to simplify the complex rate equations that govern this kinetic model into eqs 2 and 6, two key assumptions can be made. First,  $K_{eq} \gg K_{eq}'$ ; Schrock et al. report that they have never observed  $\alpha/\beta$  metallacycles B', even for alkenes that give exclusively the "head-to-tail" dimer (here denoted as "minor" isomer) that would result from decomposition of B'.<sup>13c,d</sup> Second, product displacement by substrate is rapid and quantitative. Alkene ligand exchange at Cp\*TaCl<sub>2</sub>(alkene) complexes is known to be rapid;<sup>13c</sup> furthermore, under initial rate conditions, [substrate]  $\gg$  [product]. Applying these assumptions gives the rate law represented in eq 2 for the major isomer, which can be rearranged by taking the reciprocal of both sides and constructing a linear equation (eq 3). Thus, a double-reciprocal plot of initial rate versus initial 1-hexene concentration allows the calculation of both  $K_{eq}$  and  $k_1$  (eqs 4 and 5).

rate = 
$$\frac{k_1 K_{eq} [1-\text{hexene}] [\text{Ta}]_0}{1 + K_{eq} [1-\text{hexene}]}$$
(2)

rate<sup>-1</sup> = 
$$\frac{1}{k_1 K_{eq} [Ta]_0} [1 - hexene]^{-1} + \frac{1}{k_1 [Ta]_0}$$
 (3)

$$k_1 = \frac{1}{b[\mathrm{Ta}]_0} \quad b \text{ is intercept of line from eq 3}$$
(4)

$$K_{\rm eq} = \frac{b}{m}$$
 m is slope of line from eq 3 (5)

A similar treatment can be applied to the formation of the minor isomer (eqs 6–9). This method cannot separate  $K_{eq}'$  and  $k_{2}$ , and only the product of these two values can be calculated

(eq 8). Importantly,  $K_{eq}$  can be determined independently from both sets of data (eqs 5 and 9).

$$rate = \frac{k_2 K_{eq}' [1-hexene] [Ta]_0}{1 + K_{eq} [1-hexene]}$$
(6)

rate<sup>-1</sup> = 
$$\frac{1}{k_2 K_{eq}' [Ta]_0} [1\text{-hexene}]^{-1} + \frac{K_{eq}}{k_2 K_{eq}' [Ta]_0}$$
 (7)

$$k_2 K_{\rm eq}' = \frac{1}{m' [{\rm Ta}]_0} \quad m' \text{is slope of line from eq 7}$$
(8)

$$K_{\rm eq} = \frac{b'}{m'} \quad b' \text{is intercept of line from eq 7}$$
(9)

In order to build a kinetic profile along the lines of eqs 2-9 that is relevant in the context of tandem catalysis, we have examined the initial rates of formation of both  $C_{12}$  regioisomers over a wide range of initial 1-hexene concentrations (248–4000 mM) and temperatures (80–125 °C). Figure 4 is a



Figure 4. Initial rate of formation of the major regioisomer from dimerization of 1-hexene (248–4000 mM) catalyzed by 1 (8 mM) at 100  $^{\circ}$ C (each line generated by linear regression of an overlay of at least three runs).

representative example of the data generated, showing the initial rates of formation of the major  $C_{12}$  regioisomer at 100 °C over the entire concentration range examined. Each linear correlation is an overlay of 12–15 data points collected over 3 runs, and the errors on these rates have been estimated by linear regression statistics. Table 1 contains the initial rate data collected at 100 °C.

Table 1. Representative Initial Rate Data for the	
Dimerization of 1-Hexene Catalyzed by 1 at 100 °C	С

		$k_{\rm obs} \ (10^{-5} \ {\rm M \ s}^{-1})^a$		
entry	$[1-hexene]_0 (mM)$	major	minor	
1	248	5.87(10)	1.85(4)	
2	252	6.03(12)	2.00(5)	
3	412	9.53(27)	2.98(10)	
4	699	16.73(41)	5.56(15)	
5	1010	21.37(52)	6.77(19)	
6	2000	37.2(11)	12.24(38)	
7	4000	42.9(14)	13.76(48)	

<sup>a</sup>Numbers in parentheses are standard errors from regression analysis.

The data from Table 1 reveal that the dimerization rate is positive order in [1-hexene] and that the kinetics approach saturation at high [1-hexene]. A plot of  $k_{obs}$  versus [1-hexene] clearly shows this approach to saturation (Figure 5, top),



**Figure 5.** (top) Plot of initial rate  $(k_{obs})$  for 1-hexene dimerization (blue points, major isomer; red points, minor isomer) catalyzed by **1** (8 mM) at 100 °C versus [1-hexene]<sub>0</sub> (248–4000 mM; data from Table 1), indicating an approach to saturation. (bottom) Corresponding double-reciprocal plot to calculate values for  $K_{eq'}$   $k_1$ , and  $k_2 K_{eq'}$  according to eqs 2–9.

meaning that the equilibrium governed by  $K_{eq}$  is kinetically relevant up to high [1-hexene]. In fact, at low [1-hexene] (248–699 mM), the rate dependence on [1-hexene] is nearly linear, suggesting that A is the *major* Ta species.

From the rate data obtained, double-reciprocal plots were constructed for the major and minor regioisomers at each temperature; a representative plot for data at 100 °C is shown in Figure 5 (bottom). All of these plots showed excellent linear correlation (linear regression  $R^2 \ge 0.99$ ). From the regression analyses, values for  $K_{eq}$ ,  $k_1$ , and  $K_{eq}$ ,  $k_2$  have been calculated; these data are summarized in Table 2. Independent estimates of  $K_{eq}$  by <sup>1</sup>H NMR spectroscopy under catalytically relevant conditions are in excellent agreement with the values obtained from the kinetic analysis:  $K_{eq}$  (by NMR) = 2.4(3) M<sup>-1</sup> (72 °C); 0.93(8) M<sup>-1</sup> (82 °C), and 0.50(8) M<sup>-1</sup> (93 °C).<sup>18</sup>

The most striking feature of these results is that above 80 °C  $K_{eq} < 1$ , meaning that the A + 1-alkene  $\leftrightarrows B$  equilibrium favors the reactants at these higher temperatures. For example, using 8 mM catalyst at 100 °C and an initial [1-hexene] of 250 mM (tandem catalysis conditions), nearly 90% of the tantalum

Table 2. Rate and Equilibrium Constants for 1-Hexene Dimerization

entry	temp (°C)	$K_{\rm eq} ({\rm M}^{-1})^a$	$k_1 (s^{-1})^a$	$K_{\rm eq}'k_2 \ ({\rm M}^{-1} \ {\rm s}^{-1})^a$
1	72	$2.4(3)^{b}$		
2	80	$0.98(14)^{c}$	0.020(2)	0.0047(3)
		$1.01(16)^d$		
3	82	$0.93(8)^{b}$		
4	90	$0.48(12)^{c}$	0.053(11)	0.0072(4)
		$0.50(14)^d$		
5	93	$0.50(8)^{b}$		
3	100	$0.205(60)^{c}$	0.153(44)	0.0101(4)
		$0.204(93)^d$		
4	110	$0.111(52)^{c}$	0.31(18)	0.0126(3)
		$0.129(56)^d$		
5	125	$0.029(26)^c$	1.47(78)	0.0186(4)
		$0.031(28)^d$		

<sup>a</sup>Numbers in parentheses are standard errors from repeat measurements or from regression analysis. <sup>b</sup>NMR spectroscopy data. <sup>c</sup>Major isomer data.

catalyst initially exists as the alkene complex A; at 125 °C, this value is 99%. This analysis is supported by a simple colorimetric observation: an 8 mM solution of precatalyst 1, which is a Ta(III) alkene complex (A), is dark purple; upon addition of 1-hexene at 25 °C, the solution becomes orange, which indicates metallacycle (B) formation. When it is heated to reaction temperature, it becomes dark purple (A) and, upon cooling, returns to orange (B).

We have previously shown that slow addition of 1-hexene by syringe pump over 24 h to a refluxing *n*-heptane solution ( $\sim$ 98 °C) of catalysts 1 and 2 results in >95% conversion of 1-hexene and a catalyst cooperation factor of 91%. If decomposition of the tantalum catalyst was occurring during the course of these experiments, such a high degree of catalyst cooperativity would not be observed. Furthermore, we have tested the thermal stability of the tantalum catalyst over ~4 days at 125 °C. Precatalyst 1 (0.008 mmol) and an aliquot of 1-hexene (0.2 mmol) was dissolved in  $d_8$ -toluene in a J. Young NMR tube. The tube was heated to 125 °C for 12 h and analyzed by <sup>1</sup>H NMR spectroscopy, which revealed that all of the 1-hexene had been consumed. A second 0.2 mmol aliquot of 1-hexene was added, and the tube was again heated to 125 °C. This process was repeated for seven cycles, and after each 12 h time period all of the 1-hexene had been consumed. Finally, for the eighth addition, ~2 mmol of 1-hexene was added; after 12 h at 125 °C, all of the 1-hexene was consumed. Final quantification of the reaction mixture by GC revealed a total TON of 215. Importantly, only the expected products were observed  $(C_{12})$ alkenes and  $\sim 5\%$  2-hexenes), confirming that 1-hexene consumption was not due to side reactions catalyzed by decomposition products. Clearly, the temperature sensitivity of Cp\*TaCl<sub>2</sub>(alkene) complexes is not an important factor under catalytic conditions, even at low substrate concentration.

While this experiment does not confirm that *all* of the tantalum remains catalytically active during this time period, certainly enough remains after 3.5 days to convert 250 equiv of 1-hexene during the final 12 h. In addition, since 0.2 mmol of 1-hexene should be consumed fairly quickly at 125 °C (<4 h), for the majority of the 12 h heating periods only the product alkenes are present. Thus, it would appear that the product 1,1-disubstituted alkenes can also stabilize Ta(III) intermediates, even during prolonged heating. The robust nature of the



**Figure 6.** (left) van't Hoff plot (72–125 °C) for the equilibrium  $Cp*TaCl_2(1-hexene)$  (A) + 1-hexene  $\Rightarrow$   $Cp*TaCl_2(metallacycle)$  (B), with thermodynamic parameters (blue filled points, from kinetics; red hollow points, from <sup>1</sup>H NMR spectroscopy). (right) Eyring plot (80–125 °C) for the unimolecular decomposition of  $Cp*TaCl_2(metallacyclopentane)$  (B into C), with activation parameters.

Cp\*TaCl<sub>2</sub>(alkene) system is remarkable in this context: truly, this catalyst is effectively "indefinitely active" (in a dry and oxygen-free environment!) as observed previously by Schrock et al., <sup>13d</sup> under conditions even more forcing than those originally anticipated.

A second important consequence of the A + 1-alkene  $\leq B$ equilibrium is that the rate of dimerization is relatively insensitive to temperature. For example, the rate of 1-hexene consumption at an initial concentration of 248 mM increases only ~1.6-fold from 100 to 125 °C. Analysis of the equilibrium and rate constant data in Table 2 reveals the reason for this behavior. While  $k_1$  increases ~8-fold over this temperature range,  $K_{ea}$  decreases by a factor of ~5.5. This decrease in  $K_{ea}$  can be understood in simple thermodynamic terms: the equilibrium is a 2-into-1 reaction and thus should be exothermic (bond forming) and entropically disfavored. A van't Hoff analysis confirms this intuitive rationale, with  $\Delta H^{\circ} = -22(2)$  kcal mol<sup>-1</sup> and  $\Delta S^{\circ} = -16(2)$  eu for the forward reaction (Figure 6, left). Likewise, an Eyring analysis of  $k_1$  values for the unimolecular decomposition of **B** into **C** gives activation parameters of  $\Delta H^{\ddagger}$ = 26(2) kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger}$  = 6(5) eu (Figure 6, right). Thus, as the reaction temperature is raised, the equilibrium shifts back toward A + 1-alkene, reducing the steady-state concentration of **B**. This effect is offset by the increase in  $k_1$ , meaning that the overall rate of dimerization to the major isomer increases by only 1.4-fold from 100 to 125 °C with an initial [1-hexene] of 250 mM. Notably, at an initial [1-hexene] of 4000 mM, the increase in initial dimerization rate to the major isomer is 2.4fold over the same temperature range, consistent with an equilibrium shift toward B at the higher alkene concentration.

Formation of the minor isomer follows a similar trend, with an initial rate increase of ~2-fold observed from 100 to 125 °C ([1-hexene]<sub>0</sub> = 248 mM). Here, the situation is slightly more complex. Since intermediate *A* feeds into both major and minor catalytic cycles, a shift of the *A* + 1-alkene  $\leftrightarrows B$  equilibrium toward *A* would increase the amount of tantalum available to form the minor metallacycle *B'*. This effect is manifested in the rate law of eq 6: since  $K_{eq}$  is only in the denominator, as  $K_{eq}$ decreases, the rate of minor isomer formation increases. Of course,  $K_{eq}'$  and  $k_2$  are subject to the same offsetting temperature effects as  $K_{eq}$  and  $k_1$ . Even though individual determination of these values is not currently possible, the product  $K_{eq}'k_2$  has been calculated and shows a 1.8-fold increase from 100 to 125 °C (Table 2). Since this increase is slightly larger than that for the product  $K_{eq}k_1$ , it would appear that either  $K_{eq}'$  is reduced less by increasing temperature or  $k_2$ is increased more (or both). Again, at higher initial [1-hexene] (4000 mM), the rate increase from 100 to 125 °C is greater (3.1-fold). All of these factors lead to a decrease in selectivity for the major isomer as the temperature increases: upon completion, the regioisomer ratio is 3.25:1 at 100 °C and 2.35:1 at 125 °C.

The final step of the catalytic cycles in Scheme 2 is the displacement of the product alkenes by substrate, in equilibria that are favored in the forward direction (i.e.,  $K_{\text{off}}$  and  $K_{\text{off}}' > 1$ ). While these equilibria are not significant under initial rate conditions, they become important at high conversion; in other words,  $K_{\text{off}}$  and  $K_{\text{off}}$  are measures of product inhibition. While a rigorous analysis of product inhibition kinetics has not been carried out, the full mechanism including  $K_{\text{off}}$  and  $K_{\text{off}}$  terms and isomerization rates has been modeled mathematically using the calculated rate and equilibrium constants from Table 2, entry 3. The time course data from Figure 3 were fitted according to the overall mechanism from Scheme 2.19 Refinement of  $K_{\text{off}}$  and  $K_{\text{off}}'$  gives values of 4.4(6) and 2.8(9), respectively. One would expect that  $K_{off} > K_{off}'$  due to the different sterics of the two products: the minor isomer is less bulky near the C=C bond and would thus exhibit stronger binding to the Ta(III) center. However, the difference in the obtained values is not statistically significant. Since  $K_{off}$  and  $K_{off}$ are  $\sim$ 3–4, product inhibition is a factor at high conversion; modeling the data with large (>10) values for  $K_{\rm off}$  and  $K_{\rm off}$ gives a poorer correlation. The fact that the product 1,1disubstituted alkenes bind to Ta under conditions of high [product] and low [substrate] is consistent with the thermal stability experiment described previously; perhaps this product inhibition behavior contributes to catalyst longevity at elevated temperatures by stabilizing the reactive Ta(III) fragment.

In summary, there are two key features of alkene dimerization catalyzed by 1: the reaction is positive order in alkene substrate with an approach to saturation at high [1-alkene], and the rate is relatively insensitive to temperature, especially under conditions of low initial [1-alkene]. Both of these factors are a direct consequence of the A + 1-alkene  $\Rightarrow B$  equilibrium, which has  $K_{eq} < 1$  above 80 °C and  $\Delta S^{\circ} = -16(2)$  eu. From these insights, it is clear that the tantalum catalyst operates most efficiently at lower temperature and high [substrate], the exact reverse of tandem catalysis conditions;

thus, the kinetic features of transfer hydrogenation appear to be opposite to those of alkene dimerization.

Mechanistic Studies of Ir-Catalyzed Transfer Hydrogenation. In order to rationalize the striking dichotomy in optimal conditions between catalytic alkene dimerization and tandem catalytic alkane/alkene coupling, the kinetics of 1hexene/*n*-decane transfer hydrogenation catalyzed by 2 have been examined under a similar set of conditions. Many research groups, most prominently those of Jensen, Kaska, Goldman, Krogh-Jespersen, and Brookhart, have extensively studied transfer hydrogenation<sup>14–16</sup> and alkene isomerization<sup>17</sup> by pincer-iridium catalysts. This previous work establishing the mechanisms of these reactions provides an excellent framework for understanding catalytic transfer hydrogenation in our tandem system (Scheme 3); however, for alkene dimerization by 1, we required a detailed picture of the kinetics under our specific reaction conditions.

Scheme 3. Postulated Catalytic Cycles for Alkane/Alkene Transfer Hydrogenation and Alkene Isomerization Catalyzed by  $2^a$ 



<sup>a</sup>Adapted from refs 14 and 17.

Heating a solution of 1-hexene (248 mM) and 2 (5 mM) in *n*-decane leads to the generation of several products that can be analyzed by GC (eq 10). In the  $C_6$  fraction, *n*-hexane (from



transfer hydrogenation) and internal hexenes (from alkene isomerization) are observed.  $C_{10}$  alkenes are also observed

(including 1-decene), but accurate quantification of these species is not reliable due to overlap with the large signal for n-decane solvent. Therefore, the formation of n-hexane and internal hexenes has been monitored to generate initial rate data for transfer hydrogenation and alkene isomerization respectively (Table 3).

Table 3. Initial	Rate Data for	1-Hexene/n-D	ecane Transfer
Hydrogenation	and 1-Hexene	Isomerization	Catalyzed by 2

			$k_{\rm obs} \ (10^{-5} \ {\rm M} \ {\rm s}^{-1})^a$		
entry	$[1-hexene]_0 (mM)$	temp (°C)	hydrog	isom	
1	248	100	1.26(5)	1.00(4)	
2	412	100	0.753(38)	1.53(5)	
3	699	100	0.572(20)	2.31(7)	
4	1010	100	0.387(10)	2.79(6)	
5	248	125	12.4(4)	4.73(20)	
6	412	125	8.85(23)	6.30(16)	
7	1010	125	2.88(14)	11.8(5)	
-					

<sup>a</sup>Numbers in parentheses are standard errors from regression analysis.

Analysis of the initial rates of transfer hydrogenation and isomerization versus  $[1-hexene]_0$  reveals that transfer hydrogenation is inverse order in [1-hexene] from 248 to 1010 mM, whereas isomerization is positive order in [1-hexene], exhibiting saturation behavior (Figure 7). The inverse depend-



**Figure 7.** Rates of 1-hexene/*n*-decane transfer hydrogenation and 1-hexene isomerization catalyzed by **2** at 100  $^{\circ}$ C versus initial [1-hexene] (248–1010 mM). The data clearly show inverse order in 1-hexene for transfer hydrogenation and positive order in 1-hexene for isomerization (approaching saturation).

ence on [1-hexene] is consistent with previous work on cyclooctane/*tert*-butylethylene (TBE) transfer hydrogenation catalyzed by **2**: the rate is first order in [TBE] at low concentrations (where the Ir dihydride *F* is the major resting state) and inverse order at higher concentrations.<sup>16</sup> While inhibition by TBE is due to reversible oxidative addition/ reductive elimination of a vinyl C–H bond, linear  $\alpha$ -olefins (LAOs, such as 1-hexene) inhibit catalysis by competitive formation of the 1-alkene complex *G*. Indeed, *G* (where the alkene is 1-octene) is reportedly a major resting state in *n*-octane transfer dehydrogenation.<sup>14</sup> Thus, at higher [1-hexene], the equilibrium in eq 11 would be shifted toward intermediate *G*, which is not on the transfer hydrogenation cycle.

This shift in equilibrium between resting states is also consistent with the observation that the transfer hydrogenation



rate is substantially affected by temperature, increasing nearly 10-fold from 100 to 125 °C (Table 3, entries 1 and 5). The equilibrium in eq 11 is a 3-into-2 reaction, which means that the reverse direction is entropically favored; furthermore, this equilibrium is likely close to thermoneutral, since it is known that subtle changes to ligand structure can favor F or G (or a mixture) as the resting state of alkane metathesis.<sup>150</sup> Thus, an increase in temperature might be expected to shift the equilibrium toward F, which is an on-cycle intermediate for transfer hydrogenation. Furthermore, since G is also an active catalyst for alkene isomerization,<sup>17</sup> this shift should decrease the rate of isomerization relative to transfer hydrogenation. This is exactly the case, where with an initial [1-hexene] of 248 mM,  $k_{obs}(hydrog)/k_{obs}(isom)$  is 1.26 at 100 °C and 2.62 at 125 °C. Of course, temperature effects on the other steps of both catalytic cycles will influence these rates as well.

Notably, our observation that isomerization is positive order in [1-hexene], determined from initial rate data (Table 3), is in contrast to the zero-order dependence previously reported for 1-alkene isomerization catalyzed by 2, which was observed over ~2 half-lives (single run,  $[1-alkene]_0 = 100 \text{ mM}$ ; kinetics with higher  $[1-alkene]_0$  were not reported).<sup>17</sup> This reaction proceeds by a  $\pi$ -allylic mechanism with a unimolecular turnover-limiting step and thus should be zero order in [1-alkene]; however, the positive order dependence observed here can be explained by the equilibrium between resting states in eq 11. As the concentration of 1-hexene is increased, the steady-state concentration of G will increase, leading to a higher rate of alkene isomerization. Thus, increasing [1-hexene] not only inhibits transfer hydrogenation but also favors the undesirable alkene isomerization pathway. The approach to saturation for the rate of 1-hexene isomerization shown in Figure 7 is entirely consistent with the proposed<sup>17</sup> unimolecular turnover-limiting step in the  $\pi$ -allylic isomerization catalytic cycle.

Implications for Tandem Catalytic Alkane/Alkene Coupling. The diametrically opposed kinetic trends in alkene

dimerization catalyzed by 1 and transfer hydrogenation catalyzed by 2 are major factors in the homogeneous tandem catalytic coupling of 1-hexene and *n*-heptane. As for many other one-pot dual-catalyst processes, the optimal conditions for the individual catalysts do not necessarily translate into the optimal conditions for the pair.9 While catalyst 1 operates most efficiently at lower temperatures and high alkene loading, catalyst 2 works best at high temperatures and low alkene loading. Thus, in order to best match the rates of the two individual reactions, tandem catalysis is effective at a moderate temperature (100 °C) and an alkene concentration that is as low as possible. In terms of simple batch reactions, our initial optimization<sup>10</sup> led to a 1-hexene loading of  $\sim$ 250 mM (Table 4, entry 1). Raising the substrate loading to 500 or 1000 mM merely results in the production of more 1-hexene dimer, with little additional tandem catalysis observed (entries 2 and 3); this is due to the positive order dependence on [1-hexene] for 1 and the inverse order dependence on [1-hexene] for 2. Conversely, raising the temperature to 125 or 150 °C dramatically reduces catalyst cooperativity<sup>20</sup> (entries 4 and 7), due to the much stronger temperature dependence on rate exhibited by 2 relative to 1.

While increasing [1-hexene] or temperature results in a rate imbalance between the two catalysts, it is possible that increasing both of these variables would have complementary effects, allowing a higher degree of tandem catalysis at increased substrate loading. This is indeed the case, though the increase in tandem catalysis is relatively modest. For example, the amount of  $C_{13} + C_{14}$  products at an initial [1-hexene] of 1000 mM is 28 mM at 100 °C, whereas at 125 °C it increases to 46 mM, and at 150 °C it is 57 mM. Exploiting this complementary temperature and concentration effect allows for higher tandem TONs for 1 and 2 (7 and 14, respectively). Unfortunately, the cooperativity factor decreases substantially with increasing temperature, dropping to ~25% at 150 °C. This is consistent with an increase in the rate of alkene isomerization that still outweighs the increase in dimerization and transfer hydrogenation rates. Evidently, maintaining low [1-alkene] by slow addition, as previously reported,<sup>10</sup> is a more effective strategy to enable a high degree of tandem catalysis.

Styrene Dimerization and Styrene/1-Heptene Coupling Catalyzed by 1. In the catalytic coupling of 1-hexene/

				Observed products					
+				→ + R R' + R-	C <sub>12</sub> C <sub>13</sub> R' C <sub>14</sub>	$R = R' = n \cdot C_4 H_9$ $R = n \cdot C_4 H_9, R' =$ $R = n \cdot C_5 H_{11}, R' =$ $R = R' = n \cdot C_5 H_{11}$	<i>n</i> -C <sub>5</sub> H <sub>11</sub> or = <i>n</i> -C <sub>4</sub> H <sub>9</sub>		
entry	[1-hexene] <sub>0</sub> (mM)	temp (°C)	<i>n</i> -hexane (mM) <sup>b</sup>	$C_{12} (mM)^b$	$C_{13}/C_{14} (mM)^{b}$	TON for $1^{c}$	TON for $2^c$	coop. (%) <sup>d</sup>	
1	250	100	52	81	13/10	13 (3)	10 (6)	63	
2	500	100	88	193	15/10	27 (3)	18 (7)	40	
3	1000	100	87	432	18/10	58 (4)	17 (8)	45	
4	250	125	106	58	15/13	11 (4)	21 (8)	39	
5	500	125	140	162	24/14	25 (5)	28 (10)	37	
6	1000	125	161	386	32/14	54 (6)	32 (12)	38	
7	250	150	147	39	12/12	8 (3)	29 (7)	24	
8	500	150	196	120	23/14	20 (5)	39 (10)	26	
9	1000	150	296	276	42/15	42 (7)	59 (14)	24	

Table 4. Temperature and Concentration Effects on 1-Hexene/n-Heptane Coupling by 1 and  $2^{a}$ 

"See the Supporting Information for an expanded table. <sup>b</sup>Determined by GC/FID using adamantane as an internal standard; average of at least two runs. <sup>c</sup>TONs in parentheses are for production of  $C_{13} + C_{14}$ . <sup>d</sup>Reference 20.

*n*-heptane discussed up to this point, competitive dimerization of 1-hexene is prevalent; even with slow addition of 1-hexene by syringe pump, the  $C_{12}$  fraction represents ~50% of the higher molecular weight products. In an effort to minimize this side reaction, we initially examined TBE as a possible sacrificial hydrogen acceptor that would not be incorporated into the dimerization catalytic cycle, enabling the catalytic coupling of alkanes.<sup>10</sup> While we were able to achieve this with modest yield, poor conversion and suspected catalyst decomposition led us to consider other hydrogen acceptors. Styrene seemed to be an attractive alternative, since competitive alkene isomerization would not be a factor. Furthermore, the ethylbenzene generated during transfer hydrogenation could, in principle, be converted back to styrene by dehydrogenation (steam cracking), which is practiced industrially on a large scale.<sup>21</sup>

In their initial studies of stoichiometric and catalytic alkene dimerization by 1 and related complexes, Schrock et al. did not report the dimerization of styrenes.<sup>13</sup> While the Cp\*TaCl<sub>2</sub>(styrene) complex was prepared and characterized, attempts to observe metallacycles derived from two styrene units, or styrene and an aliphatic alkene, were unsuccessful.<sup>13c</sup> These observations (or rather lack thereof) were encouraging in the context of tandem catalysis, as competitive dimerization of the hydrogen acceptor (i.e., styrene) should be minimal.

In order to test the ability of 1 to dimerize styrene, we carried out control experiments under conditions similar to those used in tandem catalytic 1-hexene/*n*-heptane coupling. Heating a 500 mM solution of styrene in C<sub>6</sub>D<sub>6</sub> with 25 mM 1 to 110 °C does in fact lead to dimerization, albeit slowly ( $t_{1/2} \approx 14$  h, eq 12). By <sup>1</sup>H NMR spectroscopy and GC analysis, there is one



major product of this reaction, the "head-to-tail" dimer formed in  $\sim$ 80–90% yield (the balance is unreacted styrene and alkene isomers of the dimers). Notably, there is a complete switch in regioselectivity from reactions with LAOs: the "tail-to-tail" product in styrene dimerization is formed in only  $\sim$ 2–3% yield.

Monitoring the dimerization of styrene under conditions analogous to tandem catalysis (250 mM styrene, 8 mM 1, 100 °C) reveals first-order dependence on [styrene] up to ~3.5 half-lives, with  $t_{1/2} \approx 40$  h (Figure 8); deviation from linearity at high conversion is likely due to product inhibition, as observed for 1-hexene dimerization. This first-order dependence is consistent with a mechanism analogous to the top catalytic cycle in Scheme 2, where the equilibrium Cp\*TaCl<sub>2</sub>(styrene) + styrene  $\Leftrightarrow$  Cp\*TaCl<sub>2</sub>(metallacycle) (with equilibrium constant  $K_{\rm eq}$ ") heavily favors reactants; this is in accord with the inability to observe metallacycles derived from styrenes.<sup>13c</sup> The observed first-order rate constant  $k_{obs}$  is equal to  $K_{eq}^{"}k_3[Ta]_{0}$ , and therefore  $K_{eq}^{"}k_3 = [6.00(6)] \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  (where  $k_3$  is the rate constant for the unimolecular decomposition of the styrene metallacycle, analogous to  $k_2$  in Scheme 2). Comparing  $K_{eq}''k_3$ to the corresponding values for 1-hexene dimerization to the major and minor isomers gives a ratio of 53:17:1  $(K_{eq}k_1:K_{eq}'k_2:K_{eq}''k_3)$ , while comparing initial rates gives a ratio of 40:13:1.

The markedly slower dimerization of styrene relative to 1hexene means that styrene should be useful as a sacrificial



Figure 8. Plot of  $\ln[styrene]$  versus time for the dimerization of styrene (250 mM) catalyzed by 1 (8 mM) at 100 °C through 4 half-lives (overlay of two runs, final 160 h data point not included in linear correlation).

hydrogen acceptor in tandem catalysis; however, dehydrocoupling of styrene with the alkane is also possible. In order to determine the relative rates of LAO dimerization and styrene/ LAO coupling, a mixture of styrene (313 mM) and 1-heptene (258 mM) was converted with 1. Under initial rate conditions, 1-heptene dimerization is ~4× faster than 1-heptene/styrene coupling, while 1-heptene dimerization is ~3× *slower* than 1hexene dimerization in the absence of styrene. Clearly, the presence of styrene inhibits LAO dimerization, likely because Cp\*TaCl<sub>2</sub>(styrene) is a significant resting state.

Analysis of the GC traces of these cross-coupling experiments indicated that there are four dominant cross-products, with one major product.<sup>22</sup> If both "head-to-tail" and "tail-totail" couplings are considered, there are four possible regioisomers (eq 13); assignment of these isomers has been



carried out by GC/MS fragmentation analysis and independent synthesis.<sup>23</sup> Heating a mixture of 1-heptene and styrene in *n*-heptane (250 mM each) with 1 (8 mM) to 100 °C for 18 h results in complete consumption of 1-heptene and ~47% conversion of styrene. The cross-products are formed in 23% yield (based on 1-heptene): the two "tail-to-tail" isomers comprise 2% each, and the "head-to-tail" isomers combined account for 19%.

Styrene as a Sacrificial Hydrogen Acceptor in Tandem Catalysis. Given the slow rate of styrene dimerization observed, its use as a sacrificial hydrogen acceptor has been examined in the tandem catalytic coupling of alkanes (Table 5). Heating a 250 mM solution of styrene and precatalysts 1 and 2 (8 and 5 mM, respectively) in *n*-heptane to 100 °C for 18 h results in the formation of three sets of higher molecular weight products: styrene dimer, styrene/ $C_7$  cross-products, and  $C_{14}$ olefins (entry 1). Ethylbenzene is produced by transfer hydrogenation between *n*-heptane and styrene, leading to a

# Table 5. Evaluation of Catalyst Cooperativity in Styrene/n-Heptane Coupling by 1 and $2^{a}$



<sup>*a*</sup>See the Supporting Information for an expanded table. <sup>*b*</sup>Determined by GC/FID using adamantane as an internal standard; average of at least two runs. <sup>*c*</sup>TONs in parentheses are for production of cross-products +  $C_{14}$ . <sup>*d*</sup>Reference 20.



Figure 9. Reaction progress for entry 7 (Table 5): (left) full plot; (right) expansion of product region. Legend: blue  $\blacklozenge$ , styrene; red  $\blacksquare$ , ethylbenzene; green  $\blacktriangle$ , C<sub>14</sub>; purple  $\diamondsuit$ , cross products; orange  $\bigcirc$ , styrene dimer. Lines are drawn as visual guides only.

catalyst cooperation factor of 63%. Under these conditions, only 62% styrene conversion was observed, with the desired  $C_{14}$  alkenes as minor products. Heating this mixture for 48 h results mainly in the production of more styrene dimer and cross products, with almost no additional transfer hydrogenation observed (entry 2), indicating decomposition of the iridium catalyst.

In an effort to improve conversion and selectivity for the  $C_{14}$  products, the catalyst ratio was inverted to 5 mM 1 and 8 mM 2 (entry 3). After 18 h, 78% styrene conversion is reached, with higher selectivity for tandem products. Increasing the loading of 2 gives the  $C_{14}$  alkenes as the major products, with 89% styrene conversion and the highest TONs observed (entry 4). Further increasing the catalyst loading gives full conversion and a good degree of selectivity for  $C_{14}$  (entries 5 and 6). Catalyst loadings of 10 and 15 mM for 1 and 2, respectively, result in the highest overall yield of tandem products (70 mM, 56%), with  $C_{14}$  formed in 37% yield (46 mM) and the styrene dimer formed in only 5% yield (6 mM) (entry 6). The ratio of tandem products

to styrene dimer can be increased to 16:1 with a minor attenuation of catalyst loadings (entry 7); however, cooperativity is slightly diminished (53%). Increasing the styrene loading to 1000 mM results in mostly styrene dimerization, analogous to the behavior observed for the 1-hexene/*n*-heptane system. Unfortunately, attempts to use slow addition of styrene to allow higher TONs have been unsuccessful, likely due to the slower dimerization rates and probable catalyst decomposition. Increasing the reaction temperature further increases the selectivity for tandem catalysis over styrene dimerization to ~26:1 (entries 9 and 10), albeit with lower yield (40–42%) and cooperativity (41–42%).

In order to compare the features of this tandem reaction to the 1-hexene/n-heptane system, the runs from entry 7 have been monitored over time (Figure 9). The time course profiles reveal steady consumption of styrene, with concomitant production of ethylbenzene. In contrast to the 1-hexene/nheptane system, all three of the higher molecular weight products are formed from the very beginning of the reaction,

with initial rates that are very similar despite the much lower concentration of 1-heptene generated by transfer hydrogenation. As the reaction progresses, styrene dimerization ceases quickly while the cross products and  $C_{14}$  alkenes continue to form until styrene is completely consumed.

As previously described, the tantalum and iridium precatalysts operate independently in 1-hexene/n-heptane coupling. In order to determine if this fact holds true with styrene as the alkene partner, styrene/n-heptane transfer hydrogenation catalyzed by **2** has been monitored and the time profile compared to the tandem reaction (Figure 10).



**Figure 10.** Comparison of transfer hydrogenation progress in the conversion of styrene (blue diamonds) to ethylbenzene (red squares) for catalysis with 2 only (hollow points, dashed lines) and with 1 and 2 in tandem (filled points, solid lines; from reaction in entry 7, Table 5; values corrected for styrene converted to cross products and styrene dimer, see the Supporting Information for more details).

Unlike the case for the 1-hexene/*n*-heptane system, there appears to be a slight decrease (factor of ~1.5) in the initial rate of transfer hydrogenation during tandem catalysis; however, both reactions reach completion in virtually the same length of time. Unfortunately, due to the slow rate of styrene dimerization and competing cross-product and  $C_{14}$  formation, a direct comparison between individual and tandem reactions with precatalyst 1 cannot be made. Nevertheless, it is possible that there is a minor, reversible pathway through which the tantalum and iridium catalysts could undergo mutual inhibition in the styrene/*n*-heptane system.

### CONCLUSIONS AND OUTLOOK

In summary, we have determined the mechanistic features of the homogeneous tandem catalytic coupling of alkanes and alkenes using sacrificial hydrogen acceptors for the combined  $Cp*TaCl_2(alkene)/[PCP]IrH_2$  system. These two catalysts operate independently under tandem catalysis conditions in the 1-hexene/*n*-heptane reaction, with no kinetically relevant interactions observed. While the rate of tantalum-catalyzed alkene dimerization is positive order in 1-alkene and is relatively insensitive to increasing temperature, iridium-catalyzed transfer hydrogenation is inverse order in 1-alkene and is accelerated substantially by increasing temperature. These opposing mechanistic features highlight the difficulty in achieving efficient tandem catalysis with two closely linked catalytic cycles: the rates of the individual processes must be wellmatched, but each catalyst may operate most effectively under very different reaction conditions.<sup>9</sup> In the present system, moderate reaction temperature and slow addition of substrate is crucial to achieving high levels of catalyst cooperation. $^{10}$ 

Because the Ta/Ir system operates using sacrificial hydrogen acceptors in transfer hydrogenation, styrene has been employed as a more effective acceptor for alkane/alkene dehydrocoupling and alkane double dehydrocoupling. Tantalum-catalyzed dimerization of styrene is slow relative to styrene/1-alkene coupling and 1-alkene dimerization, which enables high selectivity for tandem catalytic products (up to 26:1 for tandem catalysis versus styrene dimerization). Unfortunately, this system appears to undergo catalyst decomposition during the long reaction times required to reach full conversion. In contrast to the 1-hexene/*n*-heptane reactions, there is a slight inhibition of transfer hydrogenation by the addition of the tantalum catalyst, which suggests the possibility of catalyst– catalyst interactions under these conditions.

Finally, while the current dual homogeneous system can operate in tandem with a high degree of cooperativity, it cannot achieve the ideal, byproduct-free upgrading process from Scheme 1. The central challenge to realizing the envisioned scheme is effecting transfer hydrogenation between the products of alkene dimerization and the alkane feed. Because the products formed by tantalum catalyst **1** are highly branched, transfer hydrogenation is both kinetically and thermodynamically unfavorable. Thus, alternate systems for alkene dimerization that give linear products are required.<sup>12</sup> Efforts are currently underway to incorporate such catalysts into a viable tandem process, as well as to develop heterogeneous dual catalysts for converting gaseous feedstocks.

# EXPERIMENTAL SECTION

**General Considerations.** Unless otherwise noted, all experiments were performed under an *argon* inert atmosphere using standard Schlenk-line, high-vacuum-line, or glovebox techniques. Transfer hydrogenation catalysis by many pincer-Ir complexes is known to be inhibited by  $N_2$ .<sup>15c</sup>

Materials. Solvents for routine syntheses (pentane, toluene, diethyl ether, THF) were dried by passage through activated alumina, degassed under vacuum by several freeze-pump-thaw cycles, and stored over activated 4 Å molecular sieves under an inert atmosphere. n-Heptane for use in catalytic reactions (HPLC grade, >99%, Sigma-Aldrich) was predried by stirring ~400 mL over CaH<sub>2</sub> (~10 g) for at least 48 h. The solvent was then vacuum-transferred onto "titanocene"<sup>24</sup> ( $\sim$ 1 g) and stirred overnight; the solution remained black-green throughout. The n-heptane was collected from this titanocene solution by a final vacuum transfer and stored under an argon atmosphere. n-Decane for use in kinetics experiments (anhydrous, >99%, Sigma-Aldrich) was stored over activated 4 Å molecular sieves under an argon atmosphere, and aliquots were filtered through a small column of activated alumina immediately prior to use in making standard solutions. 1-Hexene and 1-heptene were distilled under argon from CaH2 after stirring for several days or vacuumtransferred from LiAlH<sub>4</sub> after sitting for several months. Styrene (>99.9%, 10-15 ppm 4-tert-butylcatechol as inhibitor, Sigma-Aldrich) was stored under an argon atmosphere at -35 °C and filtered through a small column of alumina immediately prior to use in catalytic reactions in order to remove the inhibitor and trace water. Precatalysts  $\mathbf{1}^{13c}$  and  $\mathbf{2}^{25}$  are known compounds and were prepared according to published procedures.

**General Procedure for Kinetics Experiments.** The following description for the determination of initial rates of 1-hexene dimerization is representative (see the Supporting Information for detailed experimental procedures for all data collected).

Precatalyst 1 (10.0 mg, 0.0240 mmol) was dissolved in 3 mL of a standard solution of 1-hexene (248, 252, 412, 699, 1010, 2000, or 4000 mM) and adamantane internal standard (~25 mM) in *n*-decane in a 4

mL screw-top vial. The vial was sealed with a Teflon-lined screw cap. The mixture was heated briefly with a heat gun and stirred vigorously to dissolve the precatalyst and ensure a homogeneous solution. The solution was then split into 15 aliquots of 0.2 mL each in 15 separate 4 mL vials containing stir bars. These vials were sealed and stirred at 80, 90, 100, 110, or 125 °C in an aluminum block heater. At specified time intervals, (1, 2, 3, or 4 min) vials were removed from the heat block and immersed in a dry ice/acetone bath to rapidly cool the contents, and the contents were then diluted with dichloromethane to quench the reaction. These solutions were passed through a short plug of silica gel into a GC autosampler vial and analyzed by GC.

Data for each time point were collected from 3 or 4 different vials, giving 12–15 data points for each initial rate determination. The concentrations of both major and minor product isomers were plotted versus time, and the  $k_{obs}$  values were calculated by linear regression analysis (Table S1 and Figures S4, S6, S8, S10, and S12 (Supporting Information)). These data were used to generate double-reciprocal plots for each product isomer at each temperature (Figures S5, S7, S9, S11, and S13 (Supporting Information)). These plots were subject to linear regression analysis to generate slope/intercept values, which were used to calculate  $k_1$ ,  $K_{eq}$  and  $k_2K_{eq}'$  according to eqs 2–9. **General Procedure for Tandem Catalytic Reactions.** The

General Procedure for Tandem Catalytic Reactions. The following is a representative example (entry 1, Table 4). 1 (6.6 mg, 0.016 mmol) and 2 (5.9 mg, 0.010 mmol) were dissolved in 2 mL of a standard solution of 1-hexene (250 mM) and adamantane (25 mM) in *n*-heptane in a 4 mL screw-top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap. The mixture was stirred at 100 °C in an aluminum block heater for 5 h. After it was cooled to room temperature, the brown solution was diluted with *n*-heptane and passed through a short plug of silica gel into a GC autosampler vial and analyzed by GC.

**Procedure for Monitoring Dimerization of Styrene over Time.** Precatalyst 1 (6.6 mg, 0.016 mmol), styrene (53.0 mg, 0.509 mmol), and 1,3,5-trimethoxybenzene (internal standard, 1.6 mg) were dissolved in  $C_6D_6$  (2 mL). This solution was then split evenly into four J. Young NMR tubes. Initial <sup>1</sup>H NMR spectra were recorded, and then the tubes were heated to either 100 °C (two tubes) or 125 °C (two tubes) in an oil bath. After set time intervals, the tubes were removed from the oil baths and new spectra acquired until ~4 half-lives had passed. The three aromatic protons of the 1,3,5-trimethoxybenzene internal standard (~6.25 ppm) were integrated versus the terminal vinylic proton of styrene that is *cis* relative to the phenyl group (~5.6 ppm) to generate concentration versus time plots (see the Supporting Information for more details).

Procedure for Styrene/1-Heptene Coupling. Precatalyst 1 (20.4 mg, 0.050 mmol), styrene (52.1 mg, 0.500 mmol), 1-heptene (49.0 mg, 0.499 mmol), and adamantane (internal standard, 10.2 mg, 0.075 mmol) were dissolved in 2 mL of *n*-heptane in a 4 mL screw-top vial containing a Teflon-coated stir bar. The vial was sealed with a Teflon-lined screw cap, and the contents were stirred at 100 °C in an aluminum block heater. After 18 h, the vial was removed and the contents were diluted with dichloromethane to a total volume of ~4 mL. This solution was passed through a short plug of silica gel before analysis by GC and GC/MS.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Text giving full experimental procedures, tables giving expanded data, and figures giving full kinetic data and plots, spectroscopic data, and representative GC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare the following competing financial interest(s): a patent application has been filed based partially on this work.

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