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Upgrading Light Hydrocarbons via Tandem Catalysis: A Dual Homogeneous Ta/Ir System for Alkane/Alkene Coupling

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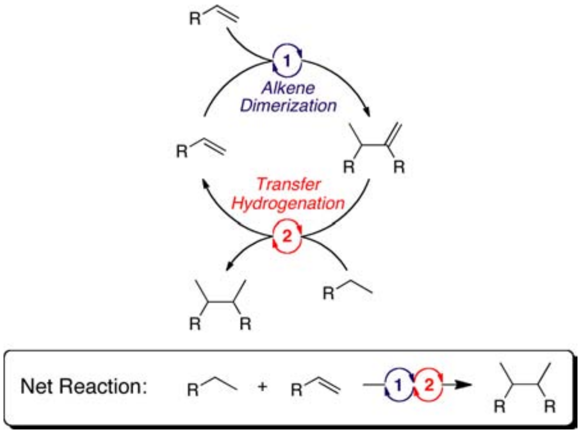
Ⓢ *Supporting Information*

ABSTRACT: Light alkanes and alkenes are abundant but are underutilized as energy carriers because of their high volatility and low energy density. A tandem catalytic approach for the coupling of alkanes and alkenes has been developed in order to upgrade these light hydrocarbons into heavier fuel molecules. This process involves alkane dehydrogenation by a pincer-ligated iridium complex and alkene dimerization by a Cp*TaCl$_2$(alkene) catalyst. These two homogeneous catalysts operate with up to 60/30 cooperative turnovers (Ir/Ta) in the dimerization of 1-hexene/*n*-heptane, giving C$_{13}$/C$_{14}$ products in 40% yield. This dual system can also effect the catalytic dimerization of *n*-heptane (neohexene as the H$_2$ acceptor) with cooperative turnover numbers of 22/3 (Ir/Ta).

Light hydrocarbons, especially those with 4−6 carbons, constitute a significant but underutilized fraction of carbon-based energy carriers.[1] Because of their volatility and low energy density, these materials cannot be used as transportation fuels on a large scale. While pure light alkenes such as ethylene and propylene are extensively used in polymer and chemical synthesis,[2] mixed alkane/alkene streams, which are unsuitable as monomers or precursors, are abundant byproducts of catalytic cracking[3] and Fischer−Tropsch synthesis.[4] Furthermore, with increased exploitation of natural gas,[5] heavy oils from bitumen and kerogen,[6] and lignocellulose,[7] the proportion of light hydrocarbons in the global energy mix will only increase. One method to turn light hydrocarbons into useful fuels would be to upgrade these feedstocks to higher-molecular-weight compounds. In this vein, alkane metathesis has emerged as a possible technology for upgrading light alkanes via combined alkane dehydrogenation and alkene metathesis; however, such a process tends to afford a statistical distribution of products, with little selectivity for a particular desired weight fraction.[8−10] While this chemistry may hold promise, a more selective method would simplify purification processes and thus increase the product yield and efficiency.

Herein we describe a complementary approach for upgrading light hydrocarbons based on a tandem alkane dehydrogenation/alkene dimerization sequence. This process takes advantage of the mixed nature of many light byproduct streams by incorporating both alkanes and alkenes as substrates. In an ideal system (shown for a linear alkane and 1-alkene in Scheme 1), one catalyst would dimerize the alkene component of the mixed feedstock to a C$_{2n}$ alkene. Subsequent transfer hydrogenation by a second catalyst would convert the alkane component to a 1-alkene while hydrogenating the C$_{2n}$ product to an alkane. The 1-alkene thus formed could then be catalytically dimerized with a second equivalent of 1-alkene, and the cycle would continue; the net reaction would be coupling of the alkane and alkene to give the higher alkane without generation of byproducts. Calculations indicate that such a reaction should be thermodynamically favored below ~250 °C;[11] therefore, the catalysts for dimerization and transfer hydrogenation must operate with appreciable rates at relatively mild temperatures.

Scheme 1. Idealized Tandem Catalytic Approach toward Alkane/Alkene Upgrading



The present work represents our initial efforts to develop such an upgrading scheme, involving a dual homogeneous catalytic system in which the tantalum catalyst Cp*TaCl$_2$(alkene) (**1**) (Cp* = C$_5$Me$_5$) effects alkene dimerization[12] and alkane/alkene transfer hydrogenation is carried out by an iridium catalyst (**2**).[8b,10,13] We demonstrate that these two species function in tandem to effect alkane/alkene coupling, although the complete synthetic cycle has not yet been fully achieved.

Often the major challenge in developing a tandem catalytic process is catalyst compatibility, particularly in homogeneous reactions.[8b,14] In the present case, alkane/alkene transfer hydrogenation requires high temperatures and relatively long reaction times to achieve high conversion. Pincer-ligated iridium catalysts are the current state-of-the-art homogeneous systems for these transformations and have demonstrated applicability in tandem reactions, namely, alkane metathesis with group-6 cocatalysts.[8b,10]

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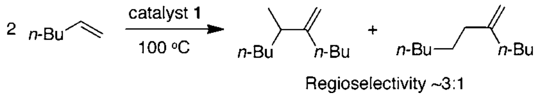
While these Ir catalysts are reported to be active at temperatures as low as 100 °C,[13] many alkene dimerization catalysts are temperature-sensitive with short lifetimes.[15] Furthermore, Ir—pincer catalysts are known to be very sensitive to trace impurities, including Lewis acids such as BR_3 (and even N_2!),[13] whereas many alkene dimerization systems require strong Lewis or Brønsted acid activators, such as methylaluminoxane (MAO) or other group-13 compounds.[15,16] Finally, deactivation of one or both catalysts by ligand transfer is a concern; for example, Ir—pincer catalysts are known to undergo chloride ligand transfer from Grubbs-type Ru alkene metathesis catalysts, rendering them inactive.[8b]

In light of these potential complications, we chose the Ta-based alkene dimerization catalyst **1**, developed by Schrock,[12] for our first trials. Cp*TaX_2(alkene) complexes are reported to be "indefinitely active" for the selective dimerization of 1-alkenes to two regioisomers at temperatures up to 100 °C (eq 1); they are inert to internal alkenes and the product 1,1-disubstituted alkenes. Importantly, no cocatalyst or activator is required.



(1)

To demonstrate catalytic alkane/alkene coupling, we examined the conversion of a 1-hexene/*n*-heptane mixture in the presence of the Ir transfer hydrogenation catalyst (*t*-Bu_4[POCOP]-Ir(C_2H_4) (**2a**)[13d] or *t*-Bu_4[PCP]IrH_4 (**2b**)[13a] and Cp*$TaCl_2$-(C_2H_4) (**1**)[12c] (Figure 1); the formation of C_{13} and C_{14} products here would signal the operation of tandem catalysis.

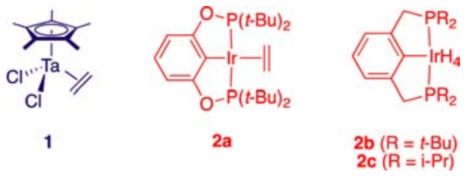
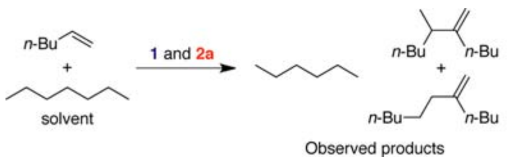


Figure 1. Precatalysts investigated for tandem catalysis.

Heating a solution of [POCOP]Ir catalyst **2a** and **1** in 1-hexene/*n*-heptane (250—1300 mM alkene) under a range of reaction conditions (100—150 °C, 1—48 h, Ta:Ir = 1—3:1) gave no measurable amount of C_{13} or C_{14} products; however, it is evident from GC analysis of the resulting hydrocarbon mixture that both catalysts did operate: nearly all of the 1-hexene was consumed, with *n*-hexane and C_{12} hexene dimers as the major observed products (eq 2 and Figure S5[11]). *n*-Hexane resulted



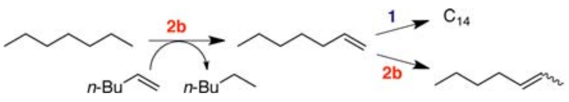
(2)

from Ir-catalyzed transfer hydrogenation, while the C_{12} products formed via Ta-catalyzed 1-hexene dimerization. Hence, deactivation caused by catalyst incompatibility is not responsible for the lack of cooperation. Instead, we hypothesize, as have others,[8b,17] that catalyst **2a** is not selective for 1-alkene formation, resulting in an overall concentration of 1-heptene that was too low for catalyst **1** to incorporate; internal heptenes, which are not dimerized by catalyst **1**, were therefore the other hydrogen transfer products.[18]

In contrast, use of the known terminal-selective[13c] Ir catalyst **2b** (10 mM) with **1** (16 mM) afforded *n*-hexane, internal hexenes, and C_{12}, C_{13}, and C_{14} alkenes; the latter two products were formed in a combined yield of 22% (Table 1, entry 1). [The identities of the C_{12}/C_{13}/C_{14} products were confirmed by comparison to a product mixture resulting from codimerization of 1-hexene and 1-heptene by **1** (Figure S4).[11]] Thus, this dual catalyst system can incorporate the *n*-alkane solvent into the dimerization cycle, demonstrating the feasibility of the proposed tandem catalytic process. Under these reaction conditions, the catalysts exhibited a "cooperativity"[19] of 35%. The full synthetic cycle of Scheme 1 was not completed, however, as no C_{12}/C_{13}/C_{14} alkanes were observed; separate control experiments showed that the 1,1-disubstituted alkene isomers afforded by **1** are poor acceptors for hydrogen transfer promoted by **2b**.

To assess the factors that influence the efficiency of this tandem Ta/Ir system, a number of reaction parameters were varied (Table 1). Reducing the catalyst loadings to 8 and 5 mM for **1** and **2b**, respectively, improved the overall turnover number (TON) without sacrificing product yield or cooperativity (entry 2). Decreasing the reaction temperature to 100 °C dramatically improved the cooperativity (63%) with a slight reduction in yield (entry 3), while altering the **1**/**2b** ratio (entries 4 and 5) was detrimental to the cooperativity. Notably, increasing [1-hexene] to 1000 mM merely resulted in the production of more C_{12} dimer (entry 6); the absolute amounts of C_{13} and C_{14} were nearly identical to those obtained with 250 mM 1-hexene (entry 3). Another intriguing observation is that in most cases the amounts of C_{13} and C_{14} were very similar. One would expect the C_{13} codimer to be the major C_7-containing species in view of the large excess of 1-hexene present relative to the amount of 1-heptene generated.

Together, these two observations suggest that most of the tandem catalytic productivity occurs only after high conversion, when [1-hexene] is low. To confirm this, the reaction from entry 3 of Table 1 was monitored over time (Figure 2). Initially, 1-hexene was rapidly consumed and transformed mainly into C_{12} by homodimerization. The C_{13} product formed slowly, and the C_{14} dimer did not form to a significant degree until nearly three half-lives had passed; more than half the amount of C_{14} was generated after >98% of the 1-hexene was consumed. These results indicate that the relative rates of dimerization and dehydrogenation are best matched at low [1-alkene], in accord with previous observations that high alkene concentrations inhibit transfer hydrogenation.[13] In addition, competitive alkene isomerization is minimized at low [1-alkene]; isomerization reduces the catalyst cooperativity by converting 1-heptene into internal heptenes that do not undergo dimerization (eq 3).

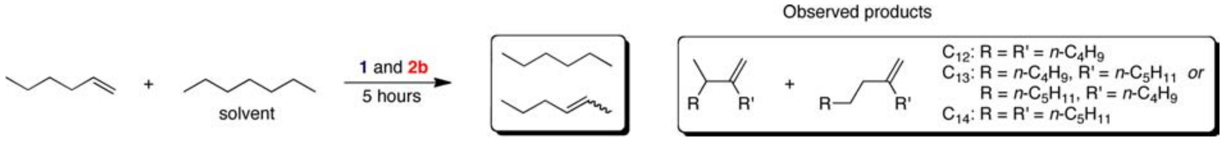


(3)

Importantly, control experiments showed that the initial rates of dimerization and transfer hydrogenation in the tandem catalytic reaction are identical to the catalytic rates exhibited by the corresponding catalysts operating separately (Figure S8).[11] This indicates that the two catalysts truly operate independently in solution under these conditions, with no mutual inhibition or deactivation.

The reaction profile in Figure 2 indicates that better C_{13}/C_{14} yield, catalyst cooperativity, and TONs might be achieved by maintaining a steady, low concentration of 1-hexene.

Table 1. Evaluation of Catalyst Cooperativity in 1-Hexene/*n*-Heptane Coupling by 1 and 2b[a]



entry	[1-hexene]$_0$ (mM)	[**1**]/[**2b**] (mM)	*T* (°C)	*n*-hexane (mM)[b]	C_{12} (mM)[b]	C_{13}/C_{14} (mM)[b]	TON for **1**[c]	TON for **2b**[c]	coop. (%)[d]
1	250	16/10	125	112	57	14/13	5 (2)	11 (4)	35
2	250	8/5	125	106	58	15/13	11 (4)	21 (8)	39
3	250	8/5	100	52	81	13/10	13 (3)	10 (6)	63
4	250	5/5	100	78	75	13/9	19 (4)	15 (6)	41
5	250	12/5	100	53	85	9/8	8 (1)	11 (5)	47
6	1000	8/5	100	87	432	18/10	58 (4)	17 (8)	45
7	1200[e]	8/5	98[f]	329[g]	293	181/59	67 (30)	66[g] (60)	91[g]

[a] See the Supporting Information for an expanded table. [b] Determined by GC/FID using adamantane as an internal standard; values are averages of at least two runs. [c] TONs in parentheses are for the production of C_{13} + C_{14} (**1**) and the total 1-heptene incorporated into C_{13} and C_{14} (**2b**). [d] Defined as in ref 19. [e] 1-Hexene was added at ~50 mM h^{-1} over 24 h, and the total reaction time was 32−36 h; ~95% conversion. [f] The reaction was run at reflux (*n*-heptane, bp ~98 °C) using an oil bath at 120 °C. [g] Estimated on the basis of mass balance (see the Supporting Information for details).

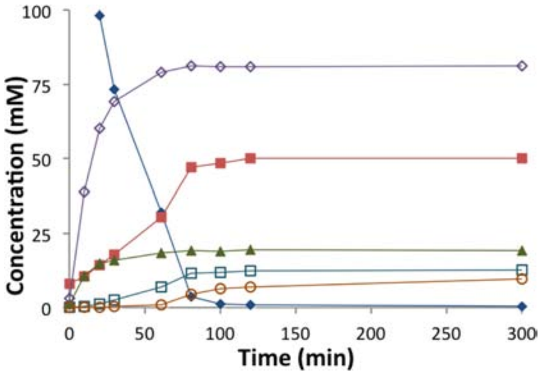
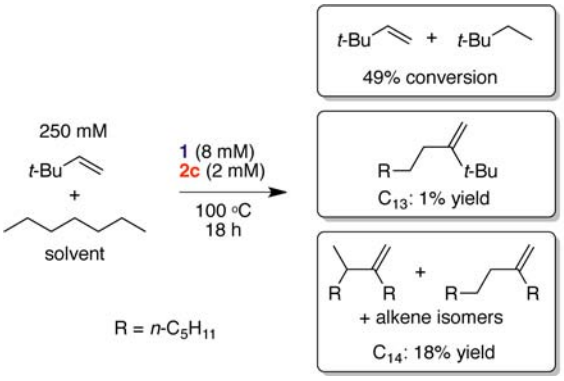


Figure 2. Reaction progress for entry 3 of Table 1. Legend: blue ◆, 1-hexene; red ■, *n*-hexane; green ▲, internal hexenes; purple ◇, C_{12}; blue □, C_{13}; brown ○, C_{14}. Lines are drawn as visual guides.[20]

Indeed, when 1-hexene was added gradually via syringe pump to a refluxing *n*-heptane solution of **1** (8 mM) and **2b** (5 mM), the outcome improved dramatically (Table 1, entry 7). When the amount of 1-hexene added was equivalent to 1200 mM, the yield of C_{13} + C_{14} was 40%, corresponding to cooperative TONs of 60 for **2b** and 30 for **1** and an estimated cooperativity of 91%.[11] These results are in stark contrast to those obtained when 1000 mM 1-hexene was added all at once, where the yield of C_{13} + C_{14} was only 6% (entry 6).

A variant of this tandem catalysis is the catalytic coupling of alkanes using a sacrificial hydrogen acceptor that is inert to alkene dimerization. Neohexene is a sterically encumbered hydrogen acceptor commonly used in Ir-catalyzed alkane dehydrogenation;[13] control experiments indicated that neohexene is not dimerized by catalyst **1** at 100 °C and that its presence does not shut down catalytic dimerization of 1-heptene. A combination of the more active Ir catalyst **2c** (2 mM) with **1** (8 mM) and 250 mM neohexene in *n*-heptane at 100 °C for 18 h resulted in ~50% conversion of neohexene and the generation of C_{14} *n*-heptane dehydrogenation/dimerization products in 18% yield (eq 4). Additionally, a small amount of a C_{13} product was observed (~1% yield, mass confirmed by GC/MS), corresponding to the coupling of neohexene and 1-heptene.[11] In terms of catalyst efficiency, cooperative TONs of 22 and 3 were achieved for **2c** and **1**, respectively, with an overall cooperativity of 38%.[19]



(4)

Longer reaction times did not increase the amount of C_{14}, signaling catalyst decomposition.

In summary, we have shown that a homogeneous dual Ta/Ir catalyst system can effect both selective coupling of alkane/alkene mixtures and dimerization of alkanes to branched alkene products with a high degree of cooperation. Hydrogen transfer from alkane to dimeric alkene is the only missing step in the full upgrading process shown in Scheme 1. This final step might be accomplished by modifying the Ir catalyst and/or by selecting a different dimerization catalyst to produce less-branched alkene isomers; these latter products may be more desirable from a fuels standpoint as well. Investigations along all of these lines are currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Thermodynamic analysis, detailed experimental procedures, figures containing GC traces of product mixtures, expanded product tables, and conversion plots. 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 provisional patent application partially based on this work has been filed.

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(18) Efforts to quantify internal heptenes by GC were hampered by the large peak for the *n*-heptane reaction solvent, which obscured the peaks for many of these isomers (as determined by coinjection of 2- and 3-heptenes with *n*-heptane).

(19) Here we define "cooperativity" as the amount of heptene generated by dehydrogenation that is incorporated into C_{13} or C_{14} dimers. Since the [1-heptene] produced is equal to the [*n*-hexane] observed, the cooperativity factor is given by $([C_{13}] + 2[C_{14}])/[n\text{-hexane}]$. For the reaction in eq 4, the cooperativity is equal to $([C_{13}] + 2[C_{14}])/[\text{neohexane}]$.

(20) The initial [*n*-hexane] was not zero because of activation of precatalyst **2b**. Because the Ir tetrahydride was used, 2 equiv of 1-hexene per equivalent of catalyst was hydrogenated immediately upon mixing; since the catalyst loading was 5 mM, the initial [*n*-hexane] was ~10 mM.