

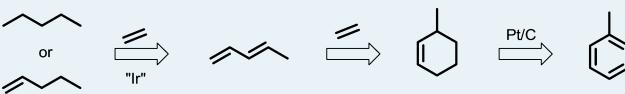
Synthesis of Piperylene and Toluene via Transfer Dehydrogenation of Pentane and Pentene

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 Supporting Information

ABSTRACT: The highly thermally stable anthraphos-based iridium pincer complex (ⁱPr⁴Anthraphos)Ir(C₂H₄) 3, was shown to catalyze transfer dehydrogenation of pentene and pentane using various olefins as acceptors in the temperature range of 160–250 °C. Using pentene itself as an acceptor, disproportionation of pentene to pentane and pentadiene was observed, but yields of (E)- and (Z)-1,3-pentadienes (piperylenes) were limited to ~25% as a result of a self-Diels–Alder reaction of the 1,3-dienes to produce isomeric mixtures of the C₁₀ dimers. Using propylene as the acceptor, higher yields of piperylenes were obtained (~40%), but self-Diels–Alder adducts were again observed along with low fractions of propylene/pentadiene Diels–Alder adducts. Using ethylene as the acceptor, the pentadienes produced via hydrogen transfer undergo an in situ Diels–Alder reaction with ethylene to produce 3-methylcyclohexene (along with toluene from further dehydrogenation) in good yields (65%). 3-Methylcyclohexene was quantitatively dehydrogenated to toluene over a heterogeneous Pd/C catalyst.



KEYWORDS: iridium pincer, catalysis, dehydrogenation, piperylene, toluene

INTRODUCTION

Catalytic transfer dehydrogenation of alkanes to produce alkenes employing iridium complexes has seen extensive development since the early reports of Crabtree^{1,2} and Felkin.^{3–5} The most robust and productive complexes discovered to date are based on iridium pincer complexes bearing bulky substituents.^{6,7} The most common acceptors used in these transfer dehydrogenation reactions are *t*-butyl ethylene and the strained alkene, norbornene.⁸ Extensive mechanistic studies have been carried out using iridium pincer complexes derived from ^tBu⁴PCP and ^tBu⁴POCOP (^tBu⁴PCP = κ^3 -C₆H₃-2,6-(CH₂P^tBu₂)₂ and ^tBu⁴POCOP = κ^3 -C₆H₃-2,6-(OP^tBu₂)₂) with cyclooctane and the substrate and *t*-butylethylene as the acceptor.^{9–15} Key steps involve the oxidative addition of the C–H bond of cyclooctane to a 14-electron iridium(I) center to yield a cyclooctyl hydride that undergoes β -hydride elimination and loss of cyclooctene to produce an Ir(III) dihydride. Hydrogenation of *t*-butylethylene closes the catalytic cycle.

Application of these catalysts to hydrocarbon conversions beyond these model systems has received increasing attention. As oil supplies diminish, new methods to transform new or less-valued carbon feedstocks into useful materials and chemical intermediates will be needed. Such feedstocks include volatile fractions of petroleum not readily used for fuels, low-carbon-number alkanes from the Fischer–Tropsch process, and shale gas-derived hydrocarbons (methane, ethane, and ethylene). A prominent application of iridium pincer complexes in this regard involves their use, in tandem with olefin metathesis catalysts, to achieve alkane metathesis in which an alkane of carbon number *n* (C_{*n*}) is converted to an alkane of higher carbon number (C_{*n+x*}) and one of lower carbon number (C_{*n-x*}). One potential application of this process is the conversion of less valuable lower-carbon-number alkanes produced by the

Fischer–Tropsch process to higher-carbon-number alkanes in the Diesel range (C₉–C₁₈).^{10,16–18}

Aromatics constitute an important class of basic building blocks currently derived from crude oil. BTX (a mixture of benzene, toluene and isomeric xylenes) is currently produced by dehydrogenating petroleum fractions using a heterogeneous “reforming” catalyst at high temperatures (>500 °C). In 2011 we reported conversion of linear alkanes to aromatics in homogeneous solution at 165 °C through transfer dehydrogenation to trienes, followed by cyclization to cyclohexadienes and further transfer dehydrogenation to yield aromatics.¹⁹ For example, heptane yields toluene, and octane leads to a mix of *o*-xylene and ethylbenzene. Four equivalents of acceptor olefin are required, which limits the practicality of this process. Building on this work, we recently reported that using an anthraphos-based iridium catalyst and ethylene as acceptor, hexene could be converted to a mix of 2,4-hexadienes and 1,3-hexadienes which, in the presence of ethylene in the same reactor, undergo Diels–Alder cycloadditions to produce the corresponding cyclohexenes. Dehydrogenation of these olefins readily occurs when passed over Pd or Pt heterogeneous catalysts to yield *p*-xylene (major product), ethylbenzene (minor product) and hydrogen.²⁰ Since hexene is commercially prepared via trimerization of ethylene, this process provides a route to *p*-xylene with ethylene as the sole feedstock. Ethane produced in the transfer dehydrogenation process can be readily cracked back to ethylene.

In an effort to expand this chemistry to other important basic chemical building blocks, we describe here our efforts directed

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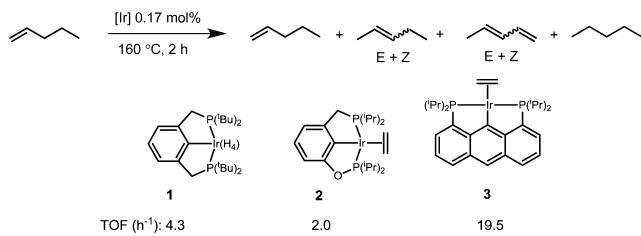


toward the dehydrogenation of pentane and pentene to 1,3-pentadiene (piperylene) and the conversion of piperylene to toluene using Diels–Alder/dehydrogenation chemistry similar to that described above. Piperylene is an important intermediate in the production of resins, adhesives, and plastics and is primarily derived from cracking of various petroleum fractions. Toluene is an important solvent and fuel additive and is used as a precursor to a wide array of other aromatic compounds. It is derived by separation from the BTX mixture described above.

RESULTS AND DISCUSSION

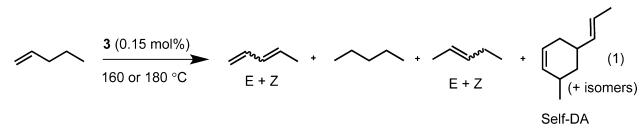
Dehydrogenation of 1-Pentene to 1,3-Pentadiene. Our initial approach to the synthesis of 1,3-pentadiene from pentene using transfer dehydrogenation was simply to employ pentene itself as the acceptor, thus effecting disproportionation of pentene to pentane and pentadiene. Olefin isomerization catalyzed by **1–3** is far more rapid than transfer dehydrogenation under these conditions, so although 1-pentene is initially added to the reactor, 1-pentene rapidly converts to a thermodynamic mixture of 1-pentene and (E)- and (Z)-2-pentenes. Three different iridium pincer catalysts shown in Scheme 1

Scheme 1. Transfer Dehydrogenation of 1-Pentene Using Pincer Iridium Catalysts



were screened for the disproportionation reaction. Reactions were conducted using dry, degassed pentene heated at 160 °C for 2 h in a closed, glass vessel together with 0.17 mol % Ir catalyst. Product concentrations were monitored by gas chromatography, and the turnover frequencies (TOFs) shown in Scheme 1 were calculated on the basis of 2 h of heating time.

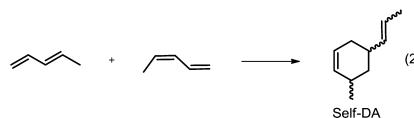
As previously observed with 1-hexene,²⁰ the anthraphos-based catalyst **3**²¹ exhibited higher catalytic activity in comparison with the more bulky *tert*-butyl-substituted catalyst, **1**, or hybrid PCOP system, **2**. Complex **3** was selected as the optimum catalyst, and disproportionation of 1-pentene with **3** was further investigated at temperatures of 160 and 180 °C at extended time intervals. These results are summarized in eq 1 and Table 1. The



distribution of products (180 °C run) as a function of time is shown in Figure 1.

Several features of these results should be noted: First, as stated above, 1-pentene isomerization to 2-pentenes occurs at a much faster rate relative to dehydrogenation to pentadiene. Second, a significant amount of pentadiene (~24%) is produced within 2 h of heating at 180 °C, whereas at 160 °C, the reaction is much slower, with only 5% diene produced. Third, as pentadiene concentrations approach ~23%, new signals appear in the C₁₀

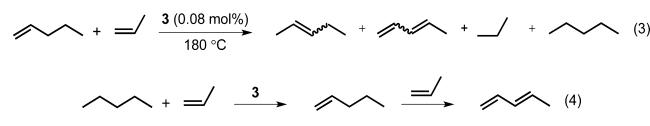
region of the GC trace and increase over time. These C₁₀ products are ascribed to “self-Diels–Alder” dimers and associated isomers from subsequent Ir-catalyzed olefin isomerization (eq 2).



To confirm these as self-Diels–Alder products, pure samples and mixtures of *trans*-1,3-pentadiene and *cis*-1,3-pentadiene were heated at 180 °C for 3 days. GC analysis showed the major products from these reactions matched the signals of products from the pentene disproportionation reactions.²² Attempts to recover piperylene via a retro-Diels–Alder reaction of the dimers at 250 °C were unsuccessful. From the data in Table 1, it is clear that when piperylene exceeds ~25 mol %, the rate of the second-order self-Diels–Alder reaction begins to compete with the transfer dehydrogenation, limiting the yield of piperylene to ~25%.

Propene as Hydrogen Acceptor. We, together with the Goldman group, previously demonstrated that propene can be used as a hydrogen acceptor in dehydroaromatization of *n*-octane.¹⁹

Here, we attempted to dehydrogenate not only 1-pentene but also *n*-pentane using propene as an acceptor (eqs 3 and 4,



respectively). Propene was liquefied in a glass tube at −78 °C and was cannula-transferred to a Parr reactor under air-free conditions. Using a 2:1 ratio of propene and pentene, significant amounts of pentadiene (23%) were generated after 2 d of heating at 180 °C, with 12% pentane also formed (entry 1, Table 2). The fraction of pentane was significantly decreased when 5 mL of propene was used, but the reaction rate decreased, most likely due to an equilibrium favoring the Ir–propene complex (entry 2, Table 2). Optimized conditions for pentadiene formation, summarized in entry 3, resulted in 79% conversion of pentene with 41% pentadiene formed. The self-Diels–Alder reaction again reduces the yield of diene monomer.

Propene also functions as a moderately efficient hydrogen acceptor in *n*-pentane dehydrogenation (eq 4, Table 3):²² 74% conversion of *n*-pentane with 40% yield of pentadienes was observed with 0.6 mol % **3** after 5.5 days at 200 °C (entry 2, Table 3), although the dehydrogenation rate is slightly slower than that for 1-pentene. The self-Diels–Alder reaction again limits the yield of diene.

The anthraphos catalyst **3** shows remarkably high thermal stability: after 2 days at 180 °C, a ³¹P NMR spectrum of the reaction mixture revealed an (anthraphos)Ir–olefin complex (δ 49.2 and 51.1 ppm) as the major component along with a small amount of Ir–CO (δ 71.6 ppm). Anthraphos Ir–CO was confirmed by comparison to an authentic sample prepared by passing CO through a solution of **3** in C₆D₆ at room temperature.

When using propene as a hydrogen acceptor, four previously unobserved peaks were detected in quite small amounts in the C-8 region of the GC trace. We reasoned these were most likely Diels–Alder adducts of propene and pentadiene. To investigate this, 1 mL of pentadiene, 10 mL of propene, and 1 mL of

Table 1. 1-Pentene Disproportionation Catalyzed by 3 at 160 and 180 °C^a

temp (°C)	time (h)	pentane (%)	1-pentene (%)	2-pentenes (%)	1,3-pentadienes (%)	self-DA (%)
160	2	5.3	17.7	71.8	5.2	0
180	2	24.2	3.2	49.0	24.2	0.4
160	19	26.1	2.7	47.1	23.4	0.8
180	17	33.7	2.6	37.1	21.0	5.6
180	130	45.5	1.9	27.9	4.4	20.3

^aReaction conditions: 0.6 mL of pentene and 3 (0.15 mol %). Reactions were monitored by GC. Numbers shown are in mol % of solution.

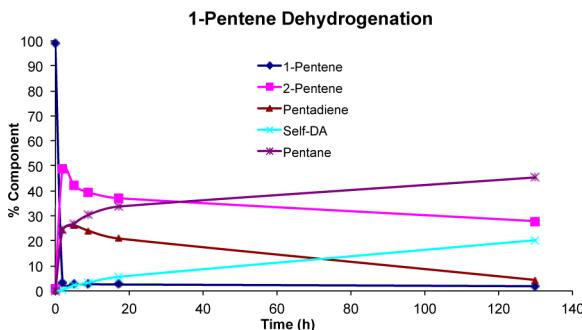
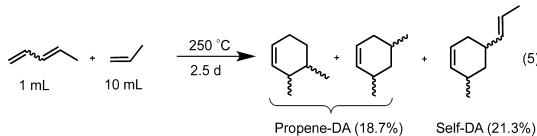


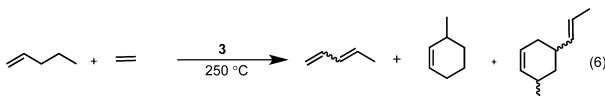
Figure 1. 1-Pentene dehydrogenation profile observed using catalyst 3 at 180 °C.

mesitylene were heated at 250 °C for 2.5 days. Propene-DA and self-DA products were detected by GC (eq 5). The



four peaks associated with propene-DA products perfectly matched those in the original transfer dehydrogenation reaction mixture.

Ethylene as Hydrogen Acceptor. Synthesis of Toluene. Similar to propene, ethylene is also an attractive choice as the hydrogen acceptor. Previously, we demonstrated that ethylene can be effectively used as the hydrogen acceptor for dehydrogenation of 1-hexene to 2,4-hexadiene and, as noted earlier, an in situ Diels–Alder reaction can lead ultimately to *p*-xylene.²⁰ Heating 1-pentene at 250 °C for 2.5 days under 250 psi of ethylene in the presence of 0.08 mol % 3 resulted in the formation of pentadiene, 3-methyl cyclohexene (ethylene-DA), and self-DA products (eq 6, entry 1, Table 4). Pentadienes



produced in the reaction, undergo an in situ Diels–Alder reaction with ethylene, providing 3-methyl-1-cyclohexene (ethylene-DA).

Table 2. Propene As Hydrogen Acceptor for 1-Pentene Dehydrogenation Catalyzed by 3^a

entry	propene used (mL)	time (d)	1-pentene (%)	2-pentenes (%)	1,3-pentadienes (%)	pentane (%)	propene-DA (%)	self-DA (%)
1 ^b	2	2	4.4	60.8	23.0	12.3	0	0.3
2 ^b	5	3.5	4.7	76.6	18.2	0.7	0	0
3 ^c	3	2	2.1	24.4	40.9	4.1	1.4	27.4

^aReaction conditions: 1 mL of pentene (9.1 mmol), propene (14.6 mmol) and 2 mL of mesitylene. ^b3 (0.08 mol %), 180 °C. ^c3 (0.3 mol %), 200 °C. Numbers shown are in mol % of solution.

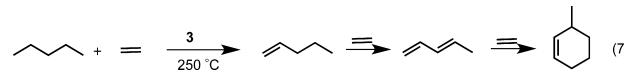
Table 3. Propene as Hydrogen Acceptor for *n*-Pentane Dehydrogenation Catalyzed by 3^a

entry	1-pentene (%)	2-pentenes (%)	1,3-pentadienes (%)	pentane (%)	propene-DA (%)	self-DA (%)
1 ^b	1.6	24.5	26.4	42.1	0	5.6
2 ^c	0.9	11.1	40.3	26.5	1.9	9.8

^aReaction conditions: 1 mL of pentane (9.1 mmol), 2 mL of propene (29.2 mmol), 4 mL of mesitylene. ^b3 (0.3 mol %), 200 °C, 5.5 d. ^c3 (0.6 mol %), 200 °C, 5.5 d. Reactions were monitored by GC, and numbers shown are in mol % of solution.

Remarkably, good conversion of pentene to 3-methyl-1-cyclohexene was observed using 600 psi of ethylene and 0.3 mol % 3 (entry 3, Table 4). At this high ethylene pressure, formation of the self-DA dimers was minimal and the ethylene-DA adduct was the major product. The anthraphos catalyst showed remarkably high thermal stability under these conditions. A 1:1 ratio of 3 and Ir–CO was detected in the ³¹P NMR spectrum of the reaction mixture after 5.5 days of heating at 250 °C.

Ethylene was also effective as a hydrogen acceptor for the dehydrogenation of *n*-pentane (eq 7, Table 5). Heating



n-pentane at 250 °C for 6.5 days with 200 psi ethylene in the presence of 0.18 mol % 3 resulted in 35% conversion of *n*-pentane (entry 2, Table 5). With 0.32 mol % 3, 74% conversion of *n*-pentane to dehydrogenated products was observed (entry 3, Table 5). In the case of 1-pentene under 600 psi ethylene in the presence of 0.3 mol % 3, a significantly higher amount of dehydrogenation products was observed, but under similar conditions with *n*-pentane, only 4% dehydrogenation products was detected after one day (entry 4, Table 5). This is most likely the result of either the stronger binding affinity for alkenes to the Ir catalyst compared with alkanes or the lower barrier for allylic C–H bond activation.

Toluene via Dehydrogenation of 3-Methyl-1-cyclohexene. Toluene was synthesized by dehydrogenating 3-methyl-1-cyclohexene (MCH) under both homogeneous (eq 8) and heterogeneous (eq 9) conditions. Table 6 summarizes the results for four iridium pincer catalysts that were screened

Table 4. Ethylene As Hydrogen Acceptor for Dehydrogenation of Pentene Catalyzed by 3 at 250 °C

entry	time (d)	1-pentene (%)	2-pentenes (%)	1,3-pentadienes (%)	pentane (%)	ethylene-DA (%)	toluene (%)	self-DA (%)
1 ^a	2.5	8.8	63.3	5.9	3.6	8.9	0	9.5
2 ^b	5.5	6.2	66.2	1.4	3.3	13.8	0	9.2
3 ^c	1	9.4	62.0	16.3	0	11.8	0.3	0.4
	2	4.5	46.0	13.5	0	26.6	2.1	4.3
	5.5	1.5	19.0	2.5	0	57.9	6.9	10.6

^a1 mL of pentene (9.1 mmol), 3 mL of mesitylene, 250 psi ethylene, 3 (0.08 mol %). ^b3 mL of pentene, 3 mL of mesitylene, 250 psi ethylene, 3 (0.08 mol %). ^c1 mL of pentene (9.1 mmol), 3 mL of mesitylene, 600 psi ethylene, 3 (0.3 mol %). Reactions were monitored by GC, and numbers shown are in mol % of solution.

Table 5. Ethylene As Hydrogen Acceptor for N-Pentane Dehydrogenation at 250 °C

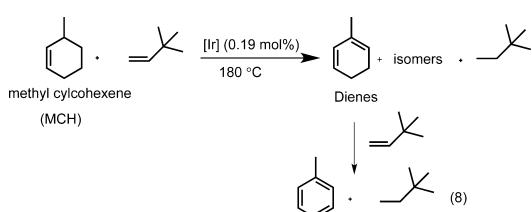
entry	[3] mol %	time (d)	pentane (%)	pentenes (%)	1,3-pentadienes (%)	ethylene-DA (%)	toluene (%)	self-DA (%)
1 ^a	0.09	9	80.4	12.6	0.7	5.7	0.7	0.5
2 ^a	0.18	6.5	65.0	18.8	5.2	10	1.5	0.1
3 ^b	0.32	6	35.4	17.7	2.5	4.5	2.0	36.5
4 ^c	0.30	1	95.6	3.0	0	0	0.4	0
5 ^c	0.30	10	79.6	9.4	0	4.4	0.7	2.3

^a1 mL of pentane (8.7 mmol), 3 mL of mesitylene, 200 psi ethylene. ^b1 mL of pentane (8.7 mmol), 2 mL of mesitylene, 250 psi ethylene. ^c1 mL of pentane, 2 mL of mesitylene, 600 psi ethylene. Reactions were monitored by GC, and numbers shown are in mol % of solution.

Table 6. Dehydrogenation of 3-Methylcyclohexene Using *tert*-Butyl-ethylene As Acceptor^a

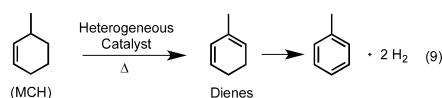
catalyst	time (h)	MCH (%)	dienes ^b (%)	toluene (%)
3 (iPr ⁴ AN)Ir	1	0.6	1.4	98
2 (iPr ⁴ PCOP)Ir	1	50.6	4.7	44.7
	2	30.7	3.8	65.5
	5.5	25	2.8	72.2
1 (tBu ⁴ PCP)Ir	1	80.1	9.9	10.3
	2	77.2	11.9	10.9
	5.5	76.5	9.5	13.8
4 (tBu ⁴ POCOP)Ir	1	92.6	7.4	0
	2	91.9	7.9	0.3
	5.5	91.2	8.4	0.4

^aReactions were monitored by GC. Numbers shown are in mol % of solution. ^bIsomer mix of methylcyclohexadienes.



for dehydrogenation of the 3-methyl-1-cyclohexene to toluene using *tert*-butyl-ethylene (TBE) as the hydrogen acceptor. Degassed 3-methyl-1-cyclohexene and TBE were heated at 180 °C using 0.19 mol % catalyst in a closed glass vessel, and the reaction was monitored by GC. The more bulky *tert*-butyl-substituted catalysts, 1 and 4, exhibited poor catalytic activities. The less bulky isopropyl-substituted catalysts, 2 and 3, showed good activities, but 3 was found to be more efficient than 2.

Dehydrogenation of cyclohexene to benzene using heterogeneous catalysts has been extensively studied.^{23–25} Recently, we reported the synthesis of *p*-xylene by dehydrogenation of *cis*-3,6-dimethylcyclohexene using commercial heterogeneous catalysts, such as Pt/C, Pt/Al₂O₃, and Pd/C. In this study, 3-methyl-1-cyclohexene was passed over a heterogeneous cata-



lyst bed at temperatures between 300 and 400 °C in the vapor phase using nitrogen as the carrier gas (eq 9). The products were trapped using liquid nitrogen and analyzed by GC. At 400 °C, both Pt/C and Pt/Al₂O₃ gave good conversions of 3-methyl-1-cyclohexene (entries 1 and 3, Table 7). Surprisingly,

Table 7. Dehydrogenation of 3-Methylcyclohexene Using Heterogeneous Catalysts^a

entry	catalyst	temp (°C)	MCH (%)	dienes (%)	benzene (%)	toluene (%)
1	Pt/Al ₂ O ₃	400	0	2.7	27.6	69.7
2	Pt/Al ₂ O ₃	450	0	0.8	53.6	45.6
3	Pt/C	400	0	1.0	1.3	97.7
4	Pt/Al ₂ O ₃	300	0.1	12.5	1.5	85.9
5	Pt/C	300	0	0	0	100
6	Pd/Al ₂ O ₃	300	0.3	18.3	2.4	79.0
7	Pd/C	300	0	3.9	3.9	92.3

^a0.6 g MCH passed over the hot catalyst (5 g, 5% metal by wt), using N₂ as the carrier gas, over the course of 2 h. Reactions were monitored by GC. Numbers shown are in mol % of solution.

benzene was detected as a side product in this reaction, with concentrations as high as 27.6% using Pt/Al₂O₃. Increased temperature led to a dramatic increase in benzene production, 53.6% at 450 °C using Pt/Al₂O₃ (entry 2, Table 7).

We suspected that cracking of the 3-methyl-1-cyclohexene in preference to toluene generated benzene. To probe this possibility, toluene was passed over Pt/Al₂O₃ at 400 °C, and only 4.5% benzene was detected, which is considerably lower than the fraction of benzene (27.6%) detected from dehydrogenation of pure 3-methyl-1-cyclohexene. Lowering the temperature to 300 °C significantly improved the yield of toluene and minimized the amount of benzene produced. Under these conditions, both Pt and Pd catalysts gave good conversion of the starting material to toluene (entries 4–7, Table 7). Pt/C at

300 °C was observed to give quantitative conversion of the starting material to toluene without production of side products (entry 5, Table 7).

CONCLUSIONS

The highly thermally stable anthraphos-based pincer iridium complex, 3, efficiently catalyzes transfer dehydrogenation of 1-pentene and *n*-pentane using propene or ethylene as the hydrogen acceptor. This work highlights the unique reactivity that can be achieved using these two readily available and recyclable hydrogen acceptors. Using propene as an acceptor, pentene/pentane dehydrogenation led to a high concentration of 1,3-pentadienes as the major products together with significant quantities of C₁₀ dimers from the self-Diels–Alder reaction of the pentadienes. In contrast, when ethylene was used as an acceptor, the 1,3 pentadienes produced undergo *in situ* Diels–Alder reactions with ethylene, providing 3-methyl-1-cyclohexene that can be quantitatively dehydrogenated to toluene and hydrogen via a common heterogeneous Pd/C catalyst.

Although applications of homogeneous iridium catalysts are not practical on a large scale, the high stability (up to 250 °C) of 3 and the ability to use ethylene as both an acceptor molecule and a Diels–Alder trap (especially in view of the expected vast increase in ethylene production from shale gas^{26–30}) suggests that supported catalysts based on 3, working in tandem with standard heterogeneous dehydrogenation catalysts, could be practical for converting C₅ feedstocks plus ethylene directly and selectively to toluene and hydrogen. This will be a focus of our future investigations in this area.

EXPERIMENTAL SECTION

General Procedures. All operations were carried out under an argon atmosphere using standard Schlenk techniques or in an argon-filled drybox. 1-Pentene, *n*-pentane, and TBE (3,3-dimethyl-1-butene) were purchased from Aldrich and were dried over Na/K alloy and collected by vacuum transfer. 3-Methyl-1-cyclohexene was purchased from TCI America Fine Chemicals, dried over Na/K alloy, and collected by vacuum transfer.

Propene and ethylene (polymer grade purity) were purchased from Airgas National Welders and used as received. Pincer complexes 1,³¹ 2,³² 3,¹⁹ and 4¹⁹ were synthesized according to literature methods. An Agilent Technologies 6850 gas chromatograph having a fused silica capillary column (100 m length × 0.25 mm i.d. × 0.50 μm film thickness) was used for gas chromatographic analysis using the following settings:

FID detector: temp = 300 °C
initial temperature: 40 °C
final temperature: 250 °C
oven program: 40 °C, hold for 20 min
ramp 1: 85 °C/min to 150 °C, hold for 5 min
ramp 2: 10 °C/min to 250 °C, hold for 20 min

Products were confirmed using authentic samples, and mesitylene was used for an internal standard.

Typical Procedure for Dehydrogenation of 1-Pentene. In an argon-filled glovebox, the appropriate iridium complex, 1-pentene (0.6 mL), and 50 μL of mesitylene were added to a 1.5 mL Kontes vial equipped with a Teflon screw cap and Teflon stir bar. The flask was sealed tightly under an argon atmosphere, and the solution was removed from the glovebox and stirred in a sand bath at the specified temperature. Periodically, the flask was removed from the bath and cooled in an ice bath.

An aliquot was removed from the flask in the glovebox with a 1 μL GC syringe and analyzed by GC. Mesitylene was used as an internal standard.

Procedure for Dehydrogenation of Pentane and Pentene Using Propene As Hydrogen Acceptor. In an argon-filled glovebox, catalyst 3, 1-pentene or *n*-pentane, and mesitylene were added to a 22 mL stainless steel Parr reactor. The vessel was sealed and taken out of the glovebox. Propene was liquefied under air-free conditions in a graduated glass tube equipped with a Teflon screw cap at -78 °C. The specified amount was carefully cannula-transferred to the precooled Parr reactor (-78 °C) under air-free conditions. The Parr reactor was then kept at room temperature for 30 min and heated in a sand bath at the specified temperature. For GC analysis, the vessel was cooled to room temperature, and the pressure was carefully released under a hood before it was opened in an argon-filled glovebox and an aliquot was removed via syringe. The vessel was then recharged with propene as described above.

Procedure for Dehydrogenation of Pentane and Pentene Using Ethylene As Hydrogen Acceptor. In an argon-filled glovebox, catalyst 3, 1-pentene or *n*-pentane, and mesitylene were added to a 22 mL stainless steel Parr reactor. The vessel was sealed, taken out of the glovebox, then pressurized with ethylene to the specified value and left at room temperature for 30 min for ethylene to saturate the solution. Once saturated, the vessel was sealed at the specified pressure and heated to 250 °C. For GC analysis, the vessel was cooled to room temperature, and the pressure was carefully released. It was then opened in an argon-filled glovebox, and an aliquot was taken via syringe. The vessel was then recharged with ethylene as described above, and heating continued at 250 °C.

Typical Procedure for Homogeneous Dehydrogenation of 3-Methyl-1-cyclohexene Using TBE. In an argon-filled glovebox, the appropriate iridium complex (0.19 mol %), 3-methyl-1-cyclohexene (0.4 mL), TBE (0.86 mL), and 40 μL mesitylene were added in a 1.5 mL Kontes vial equipped with a Teflon screw cap. The flask was sealed tightly under an argon atmosphere, and the solution was removed from the glovebox and stirred in a sand bath at 180 °C. Periodically, the flask was removed from the bath and cooled in an ice bath. An aliquot was removed from the flask in the glovebox with a 1 μL GC syringe and analyzed by GC. Mesitylene was used as an internal standard.

Dehydrogenation of 3-Methyl-1-cyclohexene Using Heterogeneous Catalysts. A Carbolite furnace with a quartz tube was filled with 5 g, 5 wt % metal loading on either Al₂O₃ or C. To one end of the furnace tube was attached a glass trap with an oil bubbler. The other end was fitted with a 14/20 ground glass joint and connected to a two-neck, 50 mL, round-bottom flask. The second neck of the flask was fitted with a septum, and N₂ was admitted to the system via a needle through this septum. The furnace was warmed to the specified temperature (300 or 400 °C) under an atmosphere of N₂ for 30 min to dry the catalyst. Following this preactivation, the glass collection trap was cooled with liquid N₂, and 1 mL of 3-methyl-1-cyclohexene added to the two neck flask. N₂ was purged through the solution at a rate of ~0.5 mL/s. After 2 h, the contents of the trap was warmed and collected. Standard (mesitylene) was added, and the solution was analyzed by GC.

Generation and Analysis of (Anthraphos)Ir(CO). A C₆D₆ solution of 5 mg of (Anthraphos)Ir(C₂H₄) (3; 8.1 μmol) in a J-Young tube was exposed to 1 atm of CO. An immediate color change from dark brown to light red was observed.

The solvent was removed under vacuum, and the resulting complex was characterized by NMR spectroscopy. ^1H NMR (600 MHz, C_6D_6): δ 7.98 (s, 1H), 7.85 (d, $J_{\text{HH}} = 6.0$ Hz, 2H), 7.33 (m, 2H), 7.27 (app t, $J_{\text{HH}} = 8.1$ Hz, 2H), 2.51 (m, $-\text{CH}(\text{CH}_3)_2$, 4H), 1.20 (m, $-\text{CH}(\text{CH}_3)_2$, 12H), 0.98 (m, $-\text{CH}(\text{CH}_3)_2$, 12H). $^{31}\text{P}\{\text{H}\}$ NMR (243 MHz, C_6D_6): δ 71.6 (s). $^{13}\text{C}\{\text{H}\}$ NMR (151 MHz, C_6D_6): 197.3 (t, $J_{\text{PC}} = 6.8$ Hz, Ir-CO), 188.9 (t, $J_{\text{PC}} = 5.3$ Hz), 151.7 (t, $J_{\text{PC}} = 10.6$ Hz), 143.8 (t, $J_{\text{PC}} = 21.9$ Hz), 132.3 (t, $J_{\text{PC}} = 6.8$ Hz), 130.8 (s), 127.1 (s), 124.9 (t, $J_{\text{PC}} = 3.8$ Hz), 121.9 (s), 27.4 (t, $J_{\text{PC}} = 14.3$ Hz, $-\text{CH}(\text{CH}_3)_2$), 19.7 ($-\text{CH}(\text{CH}_3)_2$), 18.8 ($-\text{CH}(\text{CH}_3)_2$).

■ ASSOCIATED CONTENT

■ Supporting Information

Selected gas chromatograms illustrating analysis of reaction products. 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 submitted covering technology described here.

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