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Cp*Ir-Catalyzed Acceptorless Dehydrogenation of Carbon−Carbon Single Bonds

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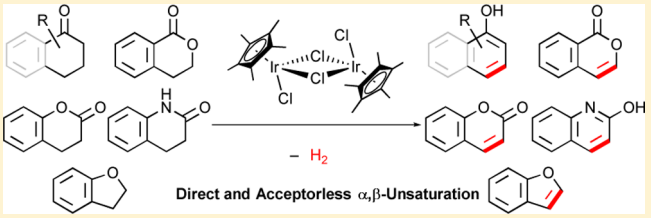
Supporting Information

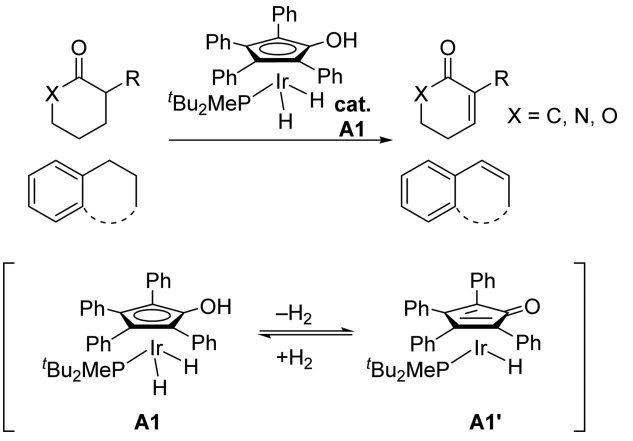
ABSTRACT: Pentamethylcyclopentadienyl (Cp*) iridium(III) chloride catalyzed acceptorless dehydrogenation of α-tetralone is reported. Cp* iridium chloride showed higher activity in comparison to other Cp* iridium complexes having bromide, iodide, or hydride or complexes without a Cp ring. The desired product, naphthol, was obtained in up to 71% yield from α-tetralone. The dehydrogenation by Cp* iridium catalyst could be applied to not only α-tetralone but also dihydrocoumarin, dihydroquinolinone, dimethylcyclohexanone, dihydrobenzofuran and 1-isochromanone, although the conversion stayed moderate. The catalytic turnover was not limited by the increased concentration of the product but by catalyst decomposition.



INTRODUCTION

Since the first preparation report in 1953,[1] cyclopentadienyl (Cp) iridium complexes have attracted great attention due to their reactivity in basic elemental reactions such as ligand substitution, transmetalation, and oxidative addition reactions.[2−4] Their catalytic activity has also been a subject of interest since the early 1970s, arising from the metal-catalyzed hydrogenation of unsaturated bonds.[4−7] After transfer[8] and acceptorless[9] dehydrogenation of alcohols were established by ruthenium complexes,[10] Cp* iridium complexes first entered the field with reports by Mashima and Tani[11] and by Ikariya and Noyori.[12] Since then, catalytic transformations involving β-hydrogen elimination from iridium alkoxides bearing a Cp ligand have been enthusiastically studied.[13−19] For the past decade the range of the applications of Cp iridium complexes has been expanded to dehydrogenation of amine[20−22] and formic acid.[23−28] Despite the momentous reports by Graham[29] and Bergman[30] on the oxidative addition of a C−H bond to a Cp iridium complex in as early as the 1980s, it was in 2013 that Cp iridium complexes first contributed to the dehydrogenation of C−C single bonds.[31] Also, there was a long interval between the development of photochemical dehydrogenation by iridium complexes[32,33] and thermal dehydrogenation by PCP pincer iridium complexes.[34−36] In 2013, we reported the first acceptorless dehydrogenation of C−C single bonds adjacent to polar functional groups such as ketone, ester, amide or a neighboring aromatic rings using iridium complexes bearing a hydroxy-substituted Cp ligand as catalysts (Schcme 1).[37] In the previously reported system, the hydroxy proton on the Cp ligand was proposed as the key for catalytic turnover. The hydride complex **A1** was proposed to undergo dihydrogen release aided by a hydroxy proton on Cp to afford cyclopentadienone complex **A1′**. Recently, a few heterogeneous catalysts were also reported to catalyze the acceptorless dehydrogenation of cyclohexanone to phenol.[38,39] Given that Cp iridium complexes are known to undergo C−H bond cleavage[29,30,40] and subsequent β-hydrogen elimination from alkyliridium species,[41,42] we hypothesized that the Cp iridium moiety itself would also have a chance to mediate the acceptorless α,β-unsaturation of carbonyl compounds. Here in this work, we found that Cp iridium chloride complex **C1** without the presence of an intramolecular hydroxy group can

Scheme 1. Dehydrogenation of C−C Single Bonds by Hydroxy-Cp Iridium Complex A1[37]



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catalyze the dehydrogenation of α-tetralone to 1-naphthol. Studies on the active species were also pursued.

RESULTS AND DISCUSSION

Dehydrogenation of α-Tetralone by Iridium Complexes. Direct acceptorless dehydrogenation of α-tetralone to 1-naphthol was reinvestigated with various iridium complexes described in Figure 1, and the results are summarized in Table 1. In addition to the dehydrogenation product **1**, naphthalene (**2**) and tetralin (**3**) were produced occasionally. Although the reaction mechanisms for the formation of **2** and **3** are unclear at this moment, the following two pathways can be proposed. (i) The C−O bond of naphthol is reduced by H_2 gas to provide naphthalene and tetralin.[43] (ii) The carbonyl group of α-tetralone is reduced to form an alcohol, which subsequently undergoes dehydration into deoxygenated products (see the Supporting Information). In all the entries for dehydrogenation of α-tetralone, the solvent cyclodecane was not dehydrogenated in significant amounts, as was confirmed by GC or ^{1}H NMR analyses.

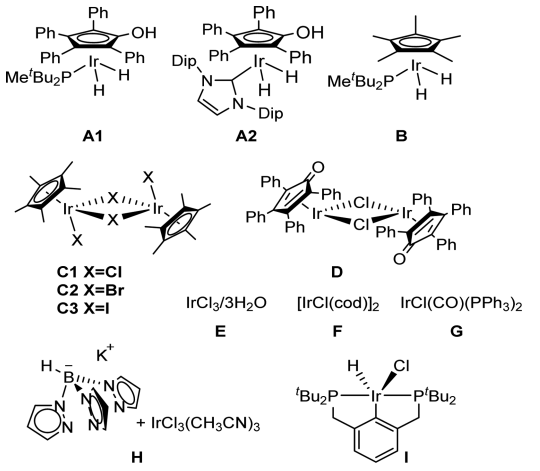
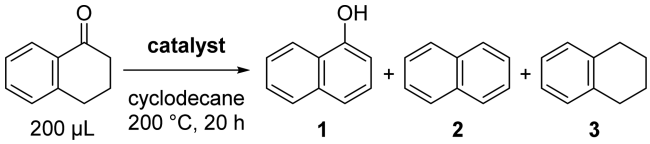


Figure 1. Iridium complexes examined for dehydrogenation of α-tetralone to 1-naphthol in this study.

Among the complexes here examined, $[Cp^*IrCl_2]_2$ (**C1**) showed the highest activity and selectivity for α-tetralone, as described below. Previously, we reported that the hydroxy group on the Cp ring was essential for the acceptorless dehydrogenation of carbonyl compounds on the basis of the fact that the corresponding Cp* complex (**B**) showed no activity in 30 min of the reaction.[37] Further investigation with **B** over an elongated reaction time, however, revealed that **B** is active in the dehydrogenation of α-tetralone to 1-naphthol after a long induction period (see the Supporting Information), which suggests that even a Cp* complex without a hydroxy group can generate active species in situ. Motivated by these results with **B**, we examined a wide range of iridium complexes. In this study, the reaction was carried out in a solvent, cyclodecane, to minimize the effect of other factors such as gas diffusion, viscosity, homogeneity, etc. In comparison to the original hydroxy-Cp iridium dihydride complex bearing di-*tert*-butylmethylphosphine (**A1**), a complex with a bulky N-heterocyclic carbene (**A2**) improved the activity while maintaining the selectivity of dehydrogenation against the reduction of C−O bonds, resulting in the selective formation of 1-naphthol in 30% yield (Table 1, entry 2). Cp* iridium dihydride complex **B** showed activity with a long induction period but the activity was poor (entry 3). The activity was dramatically improved by the use of chloride complex **C1** (47% yield, entry 4) instead of hydride complex **B**. The addition of a neutral ligand, di-*tert*-butylmethylphosphine or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) did not improve the activity of **C1** (entries 4−6). Among the Cp* iridium halide complexes **C1**−**C3** (chloride, bromide, and iodide complexes) chloride complex **C1** was most active while the iodide complex afforded only 2.0% of the desired product. In contrast to the results with Cp* complexes (entries 4 and 5) cyclopentadienone iridium chloride complex **D**, which is an analogue of **A1′** in Scheme 1 with chloride as a counteranion, showed lower activity in the absence and presence of a phosphine ligand (entries 9 and 10). The necessity of the cyclopentadienyl ring was strongly suggested in entries 11−16, since other iridium(I) or iridium(III) chloride complexes (**E**−**I**) afforded only a small amount of 1-naphthol. An improved yield was achieved by increasing the loading of iridium catalyst **C1** from 0.33 mol % (47% yield in entry 4) to 1.0 mol % (71% yield in entry 17). Hydrogen evolution was confirmed in the dehydrogenation catalyzed by complex **C1** (entry 18). Continuous purging of argon gas through the reaction mixture

Table 1. Dehydrogenation of α-Tetralone to 1-Naphthol



entry	catalyst[a]	conversn (%)[b]	yield (%)[b] 1	2	3
1	**A1**	15	13	0.3	0.3
2	**A2**	32	30	0.1	0.1
3	**B**	11	6.8	0.0	0.0
4	**C1**	59	47	1.2	0.0
5	**C1** + P^tBu_2Me[c]	25	26	0.7	0.0
6	**C1** + IPr[c]	55	38	5.5	2.9
7	**C2**	83	43	8.7	7.6
8	**C3**	16	2.0	0.3	0.1
9	**D**	4.6	4.3	0.4	0.1
10	**D** + P^tBu_2Me[c]	10	5.6	0.5	0.1
11	**E**	2.7	0.4	0.0	0.0
12	**F**	0.1	0.2	0.0	0.0
13	**G**	3.6	3.4	0.0	0.0
14	**H**[d]	1.2	0.0	0.0	0.0
15	**I**	4.6	1.0	0.0	0.0
16	**I**[e]	37	1.7	0.0	0.0
17	**C1**[f]	92	71	4.5	8.3
18	**C1**[e,g]	91	59	7.5	15
19	**C1**[e,h]	85	50	5.8	11
20	Ir colloid	4.3	0.2	1.1	0.3

[a]Reaction conditions unless specified otherwise: iridium complex (0.33 mol % as iridium metal), α-tetralone 200 μL (1.5 mmol), cyclodecane 200 μL, 200 °C, 20 h. [b]Yields were determined by GC analysis of the reaction mixture with dodecane as an internal standard. [c]Addition of 1.0 equiv of phosphine ligand or N-heterocyclic carbene ligand to iridium. [d]The catalyst was prepared in situ from potassium hydrotris(1-pyrazolyl)borate (KTp) and $IrCl_3(CH_3CN)_3$ (5 μmol each). [e]0.33 mol % of NaOtBu was added. [f]1.0 mol % of catalyst was used. [g]Hydrogen evolution was confirmed by GC analysis of the collected gas. [h]Reaction was conducted with continuous argon purging.

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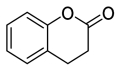
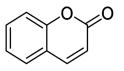
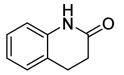
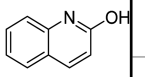
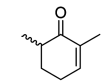
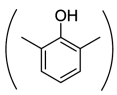
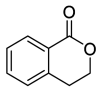
did not improve the selectivity and afforded lower naphthol yield (50%, entry 19). Only 0.2% of 1-naphthol was obtained by colloidal iridium(0) particles (entry 20), while successful acceptorless dehydrogenation of C−heteroatom and C−C single bonds was reported by using heterogeneous metal catalysts.[44−46] Complex **C1** also catalyzes the reverse reaction, the selective hydrogenation of 1-naphthol to α-tetralone, suggesting that the dehydrogenation reaction is a reversible process and that the diffusion of dihydrogen drives the reaction forward to afford 1-naphthol (see the Supporting Information).

Substrate Scope and Limitation. The catalysis by **C1** could be applied to the dehydrogenation of other six-membered cyclic carbonyl compounds such as dihydrocoumarin, dihydroquinolinone, 2,6-dimethylcyclohexanone, dihydrobenzofuran and isochromanone (Table 2). After 20 h of the reaction at 200 °C, coumarin and quinolinol were obtained in 6.0 and 25% yields, respectively, in entries 2 and 4, which is much higher than the yield obtained by hydroxy-Cp complex **A1** (0.7 and 0.2%, in entries 1 and 3). In the reaction of 2,6-dimethylcyclohexanone, in addition to dimethylcyclohexenone (3.7% yield), dimethylphenol was also obtained in 4.8% yield by complex **C1**. The activity with **C1** was not improved in comparison to **A1** in the dehydrogenation of dihydrobenzofuran or isochromanone by **C1** (entries 7−10).[47] In contrast to these five- or six-membered cyclic compounds, dehydrogenation of linear ester, methyl nonanoate, or cyclooctanone resulted in no conversion of the starting material, which is the same limitation as the reaction with hydroxy-Cp complex **A1**.[37]

Control Experiments To Elucidate Active Species. In order to shed light on the real active species, a mercury poisoning test was carried out. A drop of mercury often suppresses the catalytic activity of heterogeneous colloidal metal(0) particles by formation of amalgams.[48] The yield of 1-naphthol in the α-tetralone dehydrogenation catalyzed by $[Cp^*IrCl_2]_2$ (**C1**) was traced in the absence (a) and presence (b) of mercury, as shown in Figure 2 (the reaction conditions are the same as those of entry 4 in Table 1). The yield of 1-naphthol started to increase right after the initiation of the reaction without any induction period, which is in sharp contrast with the reaction by Cp* iridium hydride complex **B**, which required at least a 1 h induction period (see the Supporting Information). As the reaction progressed, catalyst **C1** lost its activity in 2−4 h (Figure 2a). The presence of mercury hardly affected the initial reaction rate, implying that the initial homogeneous iridium catalysis would be in operation in this Cp*iridium catalyzed reaction (Figure 2b). After 2 h, however, different behavior was observed in the presence and absence of mercury as described below: in the presence of mercury, the conversion of α-tetralone was completely suppressed. In the absence of mercury, however, even after 2 h, the conversion gradually increased and the yield of naphthalene and tetralin became significant. It could be interpreted that the homogeneous active catalyst gradually decomposed to heterogeneous species which catalyzed both the dehydrogenation of α-tetralone and the production of naphthalene and tetralin. The new heterogeneous species eventually become deactivated over a short time, since the conversion of α-tetralone gradually stopped (Figure 2a).

Effect of 1-Naphthol on the Catalytic Activity. In 2011, Goldman reported product inhibition in the iridium(I)-mediated dehydrogenation of cyclohexanone to phenol; the oxidative addition of phenol to the iridium(I) active species caused the formation of inactive iridium(III).[49] To clarify whether such product inhibition is the origin of the deactivation in our study, the reaction in entry 4 in Table 1 was carried out in the presence of additional 277 μmol (18 mol %) of 1-naphthol at the beginning of the reaction. In Figure 2c, the conversion of α-tetralone and the yield of 1-naphthol and other side products are plotted. Note that the yield of 1-naphthol is described as the difference between the total amount of 1-naphthol and the originally added amount (277 μmol). As shown in Figure 2a,c, in the first 2 h, no significant difference in the yield of 1-naphthol was observed, suggesting that an increase in naphthol concentration did not inhibit the catalysis. In Figure 2c, the yield of 1-naphthol stopped in 2−4 h while

Table 2. Substrate Scope of Dehydrogenation Catalyzed by A1 and C1

Entry	Substrate	Cat.	Conv.[d] (%)	Yield[d] (%)	
1[a]		**A1**	3.1		0.9
2[a]		**C1**	21		6.0
3[b]		**A1**	12		0.2
4[b]		**C1**	34		25
5[c]		**A1**	8.5		1.9 (0.1)
6[c]		**C1**	9.3		3.7 (4.8)
7[e]		**A1**	68		3.9
8[e]		**C1**	56		3.8
9[f]		**A1**	13		0.9
10[f]		**C1**	4.4		0.2

[a]Reaction conditions: substrate 1.6 mmol and iridium complex (0.30 mol % as iridium metal) in cyclodecane 200 μL at 200 °C for 20 h. [b]Reaction conditions: substrate 1.4 mmol and iridium complex (0.37 mol % as iridium metal) in cyclodecane 200 μL at 200 °C for 20 h. [c]Reaction conditions: substrate 1.4 mmol and iridium complex (0.34 mol % as iridium metal) in cyclodecane 200 μL at 200 °C for 20 h. [d]The conversion and yields were determined by GC analysis with dodecane as an internal standard. [e]Reaction conditions: substrate 1.3 mmol and iridium complex (0.38 mol % as iridium metal) in cyclodecane 200 μL at 200 °C for 20 h. [f]Reaction conditions: substrate 1.6 mmol and iridium complex (0.30 mol % as iridium metal) in cyclodecane 200 μL at 200 °C for 20 h.

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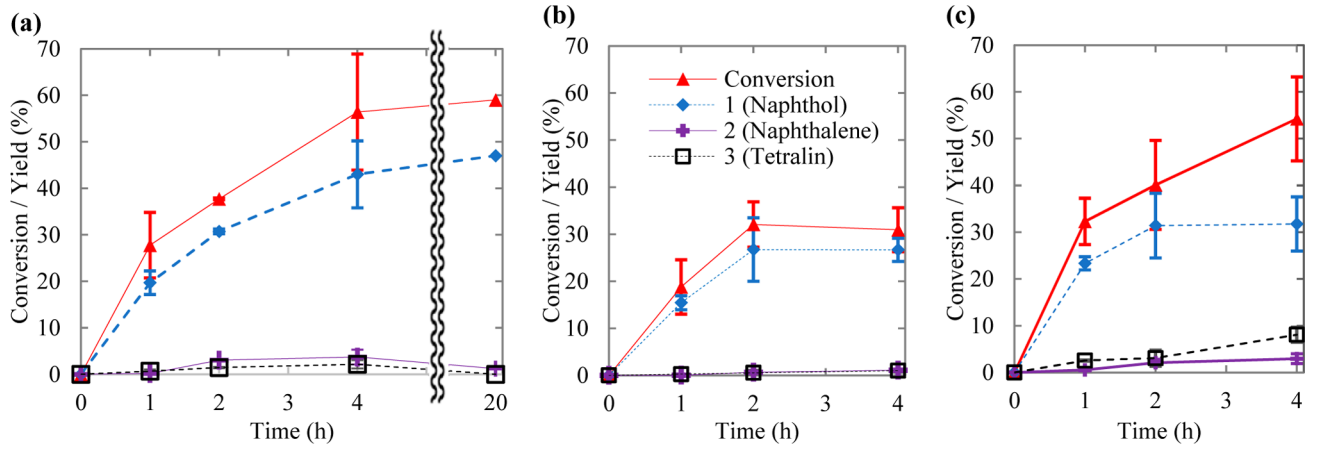

Figure 2. Time course trace of dehydrogenation of α-tetralone by $[Cp^*IrCl_2]_2$: (a) under standard reaction conditions of α-tetralone 200 μL (1.5 mmol), cyclodecane 200 μL, **C1** (5 μmol for Ir), and 200 °C; (b) with one drop of mercury at the beginning of the reaction; (c) with 277 μmol (18%) of 1-naphthol at the beginning of the reaction.

continuous consumption of α-tetralone was observed along with the production of naphthalene and tetralin, possibly due to the formation of a new active species.

CONCLUSION

In conclusion, Cp* iridium chloride complex **C1** was found to have high activity for the acceptorless dehydrogenation of α-tetralone to 1-naphthol in up to 71% yield. Dihydrocoumarin, dihydroquinolinone, 2,6-dimethylcyclohexanone, dihydrobenzofuran and isochromanone were also applied to this α,β-unsaturation. Although the mechanism of this catalysis is still unclear, the mercury test supported a homogeneous species catalyzed selective dehydrogenation in the initial stage of the reaction. As the reaction proceeded, in 1−2 h, a new species, presumably a heterogeneous one, appeared and not only catalyzed dehydrogenation of α-tetralone to 1-naphthol but also worked to form naphthalene and tetralin. The new species generated in 2 h was deactivated in an additional few hours, and thus the overall yield of 1-naphthol remained moderate. The existence of 1-naphthol, the product of the reaction, hardly affected the initial reaction rate of the dehydrogenation of α-tetralone.

EXPERIMENTAL SECTION

The following compounds were used as received: $[Cp^*IrCl_2]_2$ (Kanto Chemical Co. Inc. (Kanto)), iridium trichloride (Tanaka Kikinzoku Kogyo K.K.), $IrCl(CO)(PPh_3)_2$ (Tokyo Chemical Industry Co. Ltd. (TCI)), dihydroquinolinone (TCI), potassium hydrotris(1-pyrazolyl)-borate (TCI), mercury (Wako Pure Chemical Industries Ltd.). The following compounds were purchased from commercial suppliers and degassed by freeze−pump−thaw before use: cyclodecane (Aldrich), α-tetralone (TCI), dihydrocoumarin (TCI), 2,6-dimethylcyclohexanone (mixture of isomers, TCI). The following compounds were prepared according to the literature procedures: di-*tert*-butylmethylphosphine,[50] 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),[51] **A1**,[37] **A2**,[52] **B**,[37] **C2**,[53] **C3**,[54] **F**,[55] $IrCl_3(CH_3CN)_3$,[56] and **I**.[34] Product yields were determined with a Shimadzu GC-2014 instrument equipped with an InertCap 5MS/Sil capillary column (0.25 i.d., 0.25 μm df, 30 m) and FID detector using a calibration curve made with dodecane as an internal standard.

General Procedure for the Catalytic Dehydrogenation. Into a glass tube (i.d. = 5 mm, *L* = 15 cm) were placed a metal complex (5 μmol of iridium metal), 200 μL of substrate, and 200 μL of solvent under an argon atmosphere. The reaction vessel was capped with a rubber septum and connected to an argon line via an 18-gauge stainless needle. The tube was heated with a sand bath at 200 °C. After it was heated and stirred at that temperature for the indicated time, the reaction mixture was cooled to room temperature and diluted with acetone and dodecane was added (ca. 10 μL) as an internal standard. The resulting solution was filtered through Florisil and subjected to GC analysis.

Procedure for Mercury Poisoning Test. Into a glass tube (i.d. = 5 mm, *L* = 15 cm) were placed a metal complex (5 μmol), substrate, and solvent under an argon atmosphere. The reaction vessel was capped with a rubber septum, one drop of Hg(0) was quickly added, and the vessle was connected to an argon line via an 18-gauge stainless needle. The tube was heated with a sand bath at 200 °C. After it was heated and stirred at that temperature for the indicated time, the reaction mixture was cooled to room temperature and diluted with acetone and dodecane was added (ca. 10 μL) as an internal standard. The resulting solution was filtered through Florisil and subjected to GC analysis.

Procedure for Product Inhibition Experiments. A glass tube was charged with **C1** (2.0 mg, 5 μmol of iridium metal), substrate, solvent, and 40.0 mg of 1-naphthol. The reaction vessel was capped with a rubber septum and connected to an argon line via an 18-gauge stainless needle. The tube was heated with a sand bath at 200 °C. After it was heated and stirred at that temperature for the indicated time, the reaction mixture was cooled to room temperature and diluted with acetone and dodecane was added (ca. 10 μL) as an internal standard. The resulting solution was filtered through Florisil and subjected to GC analysis.

Preparation of Iridium Colloid.[57] In a 50 mL stainless autoclave with an inner glass tube and PTFE-coated stir bar, 16.9 mg (50 μmol for iridium) of $[IrCl(cod)]_2$ and 1 mL of benzene were charged under Ar. After pressurization with H_2 (ca. 0.2−0.3 MPa), the reaction mixture was stirred at 25 °C at 600 rpm for 1 h. Then a black colloidal dispersion was formed in benzene. The reaction mixture was degassed by purging with nitrogen for 30 min.

Procedure for the Catalytic Dehydrogenation by Iridium Colloid. In a septum-capped glass tube charged with 200 μL of cyclodecane was placed 100 μL of the iridium colloidal dispersion (5 μmol, prepared above) via syringe. With vigorous stirring, benzene was removed under dynamic vacuum for 30 min. To this catalyst dispersion in cyclodecane was added 200 μL of α-tetralone under an argon atmosphere. The reaction mixture was heated with a sand bath at 200 °C. After it was heated and stirred at that temperature for the indicated time, the reaction mixture was cooled to room temperature and diluted with acetone and dodecane was added (ca. 10 μL) as an internal standard. The resulting solution was filtered through Florisil and subjected to GC analysis.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00245.

Detail of experimental equipment and additional experimental results (PDF)

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Notes

The authors declare no competing financial interest.

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