

Supporting Information For:
**Cp*Ir-catalyzed Acceptorless Dehydrogenation of Carbon–Carbon
Single Bonds**

Hideaki Ando,[†] Shuhei Kusumoto,[†] Weiwei Wu,[‡] Kyoko Nozaki^{*,†}

[†]Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113-8656, Japan.

[‡]Department of Chemistry, Stanford University, Stanford, CA 94305, USA

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Experimental equipment

(a) entry 18 Table 1 (b) entry 19 Table 1 (c) other entries

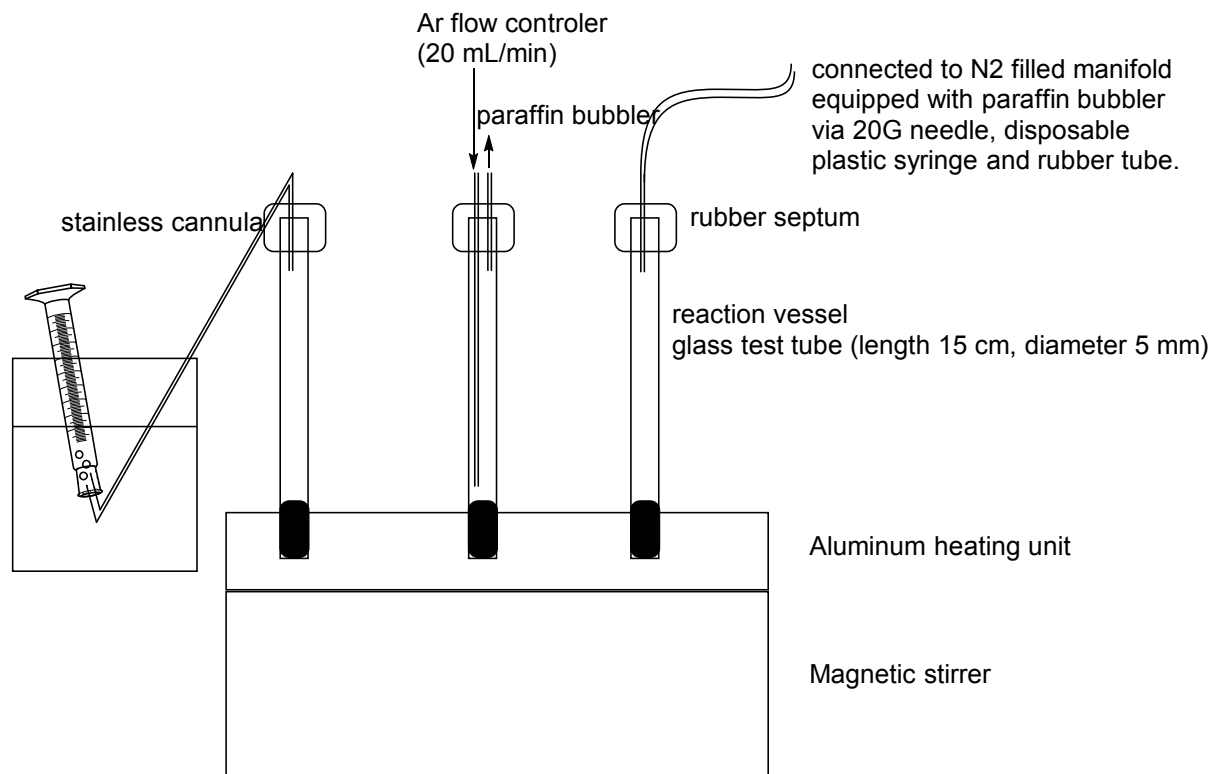
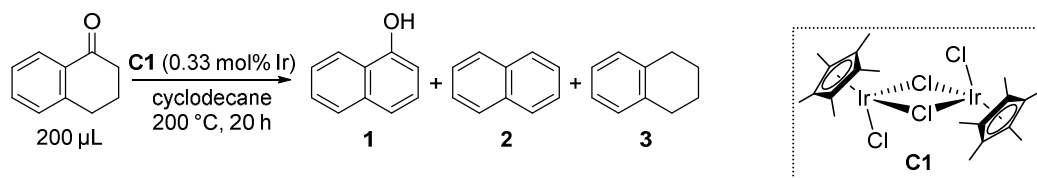


Figure S1 Experimental equipment for dehydrogenation reaction

ADDITIONAL EXPERIMENTAL RESULTS

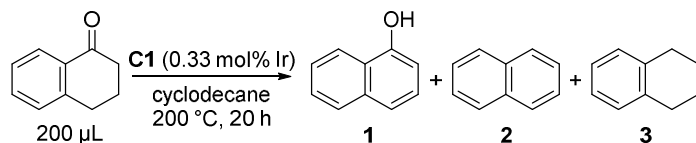
Table S1 Dehydrogenation of α -tetralone to naphthol under varied reaction temperature^a



Entry	Temperature	Conv. (%) ^b	Yield (%) ^b		
			1	2	3
1	200	59	47	1.2	0.0
2	180	44	30	6.6	3.4
3	160	15	14	0.1	1.5

^aReaction condition: Complex **C1** (0.33 mol% as Ir metal), α -tetralone 200 μ L (1.5 mmol), cyclodecane 200 μ L, 20 hours.
^bYields are determined by GC analysis of the reaction mixture with dodecane as an internal standard.

Table S2 Dehydrogenation of α -tetralone to naphthol in various solvents^a



Entry	Solvent	Conv. (%) ^b	Yield (%) ^b		
			1	2	3
1	Cyclodecane	59	47	1.2	0.0
2	hexylcyclohexane	85	58	12	2.8
3	hexylbenzene	35	29	1.7	1.4
4	2-methylbiphenyl	39	29	2.6	0.6
5	Tetraethyleneglycol dimethyl ether	64	41	7.1	8.1

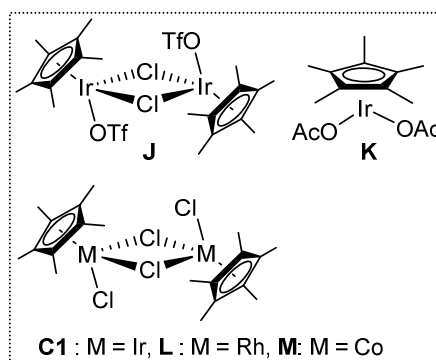
^aReaction condition: Complex **C1** (0.33 mol% as Ir metal), α -tetralone 200 μ L (1.5 mmol), solvent 200 μ L, 200 °C, 20 hours. All solvents were purchased from Tokyo Chemical Industry, Co. Ltd. (TCI) and degassed by freeze-pump-thaw before use. ^bYields are determined by GC analysis of the reaction mixture with dodecane as an internal standard.

When hexylcyclohexane was employed as solvent (entry 2), the conversion and yield of naphthol increased compared to entry 1, but at the same time hydrogenation of aromatic ring was also accelerated to produce **2** and **3**. Aromatic solvent (hexylbenzene and

2-methylbiphenyl) decreased the conversion and yield of 1-naphthol (entries 3 and 4). In ether solvent (entry 5), the conversion and yield of 1-naphthol was comparable to entry 1 albeit with lower selectivity for the production of 1-naphthol.

Table S3 Dehydrogenation of α -tetralone to naphthol with other catalysts^a

Entry	Catalyst	Conv. (%) ^b	Yield (%) ^b		
			1	2	3
1	C1	59	47	1.2	0.0
2	J	90	3.5	22	0.5
3	K	47	23	0.0	0.0
4	L	10	3.2	0.11	0.0
5	M	12	0.2	0.0	0.0

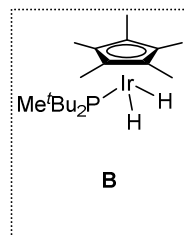


^aReaction condition: iridium complex (0.33 mol% as Ir metal), α -tetralone 200 μ L (1.5 mmol), cyclodecane 200 μ L, 200 °C, 20 hours. ^bYields are determined by GC analysis of the reaction mixture with dodecane as an internal standard.

Replacement of two chloride in complex **C** to triflate (Complex **J**) showed high conversion to give naphthalene instead of naphthol as the major product along with many kinds of products, presumably dimerized compounds after aldol condensation or oxidative coupling of aromatic rings (Entry 2 Table S3). Acetate complex **K** afforded moderate yield of 1-naphthol with formation of unidentified products in ca. 20% yield. Analogous rhodium and cobalt complexes **L** and **M** resulted in formation of only small amount of 1-naphthol formation.

Table S4 Time course dependency in dehydrogenation of α -tetralone by complex **B**: Detected induction period^a

Entry	Time (h)	Conv. (%) ^b	Yield (%) ^b		
			1	2	3
1	1	3.5	0.0	0.0	0.0
2	2	1.1	0.0	0.0	0.0
3	20	11	6.8	0.0	0.0



^aReaction condition: complex **B** (0.33 mol%), α -tetralone 200 μ L (1.5 mmol), cyclodecane 200 μ L, 200 °C, 20 hours. ^bYields are determined by GC analysis of the reaction mixture with dodecane as an internal standard.

Induction period longer than 1 hour was observed in dehydrogenation of α -tetralone by Cp*iridium dihydride complex **B**. In 1–2 hours, no 1-naphthol, naphthalene or tetralin formation was observed, while in 20 hours of the reaction, a small amount of

dehydrogenated product (1-naphthol) was observed, which implies there is a long induction period to generate catalytic active species from **B**.

Table S5 Hydrogenation of 1-Naphthol by **C1**^a

1 220 mg		α -tetralone	2	3
Time (h)	Conv(%)	Yield (%) ^b		
		α -tetralone	2	3
1	0	0.1	0	0
20	56	50	1.4	1.5

^aReaction condition: complex **C1** (0.33 mol%), 1-naphthol 220 mg (1.5 mmol), cyclodecane 200 μ L, 200 $^{\circ}$ C, under H₂ (1 atm). ^bYields are determined by GC analysis of the reaction mixture with dodecane as an internal standard.

We conducted the hydrogenation of 1-naphthol by **C1** under 1 atm of H₂. Hydrogenated product, α -tetralone was given as the major product in 20 hours, accompanied by the production of naphthalene and tetralin in trace amounts. Thus, the reversibility of dehydrogenation of α -tetralone was confirmed.

Analysis of the evolved gas in dehydrogenation of α -tetralone (entry 19, Table 1)

During the reaction, the evolved gas (6.4 mL) was collected by water displacement method and subjected to GC analysis. The ratio of dihydrogen and argon in the gas phase was determined to be 43:57. As the initially filled argon gas was 4.1 mL, the amount of evolved dihydrogen was calculated to be ca. 3.1 mL, 138 μ mol.

Reference

- (1) Kusumoto, S.; Akiyama, M.; Nozaki, K. *J. Am. Chem. Soc.* **2013**, *135* (50), 18726–18729.