

Cp* Iridium Complexes Give Catalytic Alkane Hydroxylation with Retention of Stereochemistry

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Supporting Information

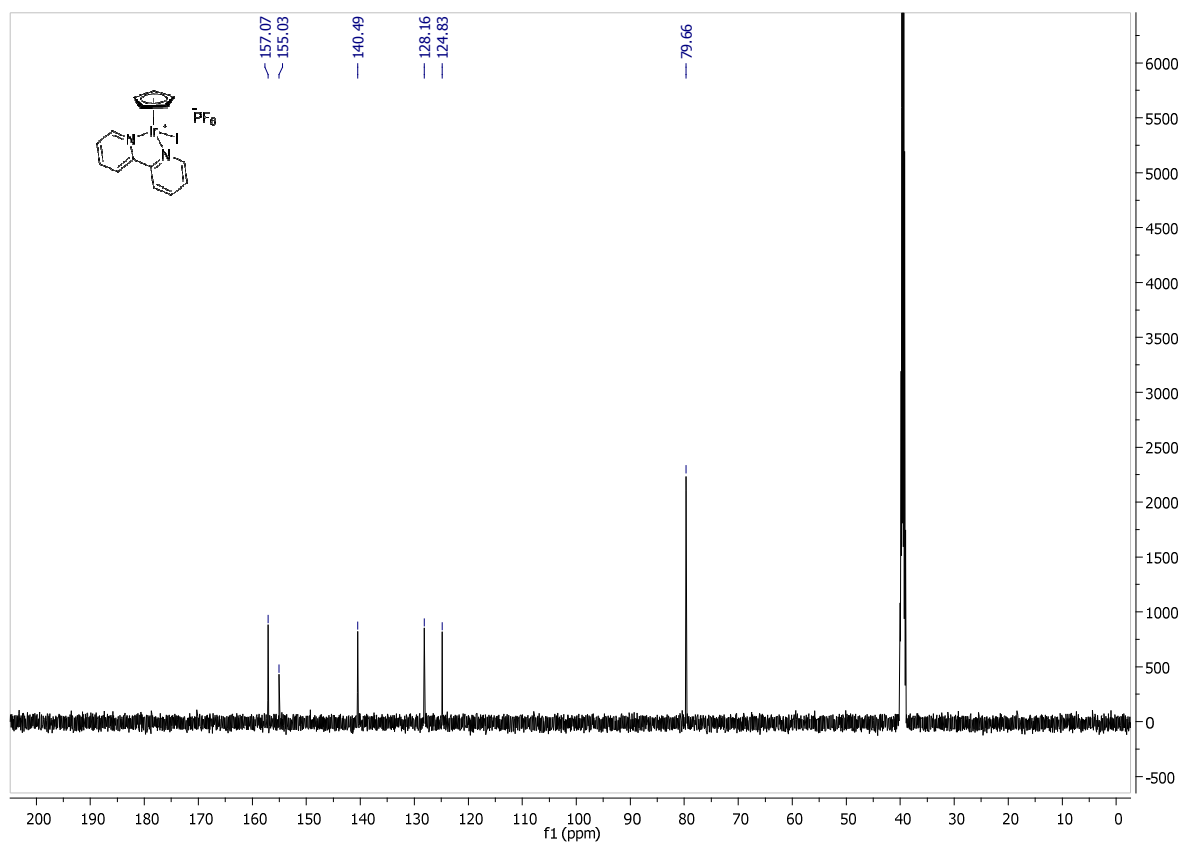
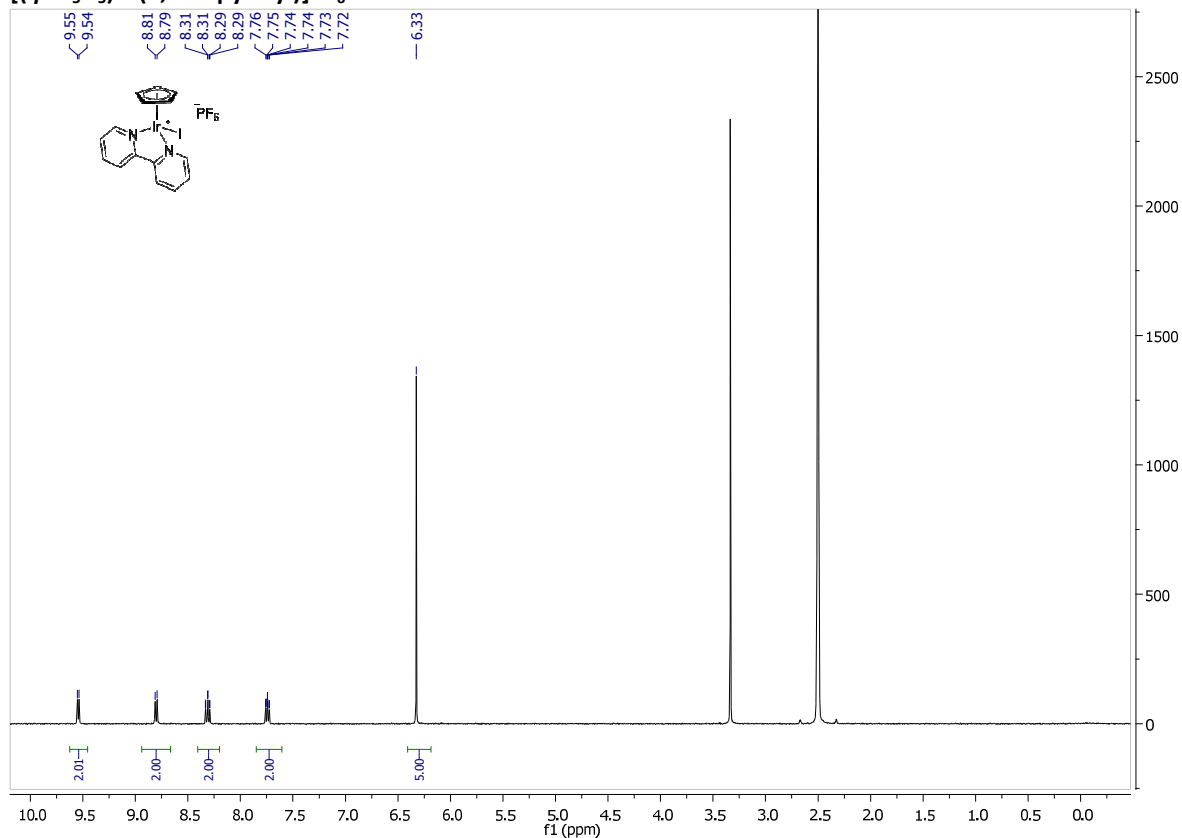
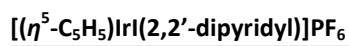
General Procedures

All solvents were of commercial grade. Reagents were purchased from major commercial sources and used without further purification. Cp*Ir complexes **1**ⁱ, **3**ⁱⁱ, **4**ⁱⁱⁱ and **5**^{iv} were prepared by literature procedures. NMR analysis was done on 400 or 500 MHz Bruker spectrometers and the chemical shift was referenced to residual solvent peak. Products of oxidation of cis-cyclooctene, ethylbenzene, cis-decalin and THF were confirmed by comparing the ¹H NMR and ¹³C NMR with the literature values.

Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{2,2'-dipyridyl})]\text{PF}_6$ (**6**)

$[(\eta^5\text{-C}_5\text{H}_5)\text{IrI}_2]_x^{\text{vi}}$ – A 50 mL flame-dried Schlenk flask was charged with $\text{CpIr}(\text{C}_2\text{H}_4)_2^{\text{v}}$ (0.215 g, 0.686 mmol) in a nitrogen-filled glove box and 30 mL dry, degassed dichloromethane was added, followed by iodine (0.185 g, 0.729 mmol). The reaction was stirred at room temperature for one hour, during which time a fine purple-brown precipitate formed in solution. The precipitate was collected by filtration in air and washed with two 5 mL portions of dichloromethane. Yield 0.272 g (78%). As previously reported, the polymeric material is insoluble in water and most organic solvents.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{2,2'-dipyridyl})]\text{PF}_6$ (**6**) – $[(\eta^5\text{-C}_5\text{H}_5)\text{IrI}_2]_x$ (0.162 g, 0.317 mmol), 2,2'-dipyridyl (0.0549 g, 0.352 mmol) and potassium hexafluorophosphate (0.0881 g, 0.479 mmol) were combined in an oven-dried 50 mL Schlenk flask under nitrogen, and 30 mL dry, degassed acetonitrile was added. The suspension was heated to 50 °C under nitrogen, gradually lightening in color until it was an entirely homogeneous solution after approximately 4 hours. After heating for 16 hours, the now-yellow solution was cooled to room temperature and reduced in volume to 1-2 mL on a rotary evaporator. Addition of 50 mL of DI-water gave a yellow precipitate which was collected by filtration in air. The solid was washed first with water, then diethyl ether, and finally dried *in-vacuo*. Yield 0.158 g (73%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.54 (d, J = 5.0 Hz, 2H), 8.80 (d, J = 8.0 Hz, 2H), 8.31 (m, 2H), 7.74 (m, 2H), 6.33 (s, 5H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 157.07, 155.03, 140.49, 128.16, 124.83, 79.66. Anal. Calcd for Ir₁I₁C₁₅H₁₃N₂P₁F₆. C, 26.29; H, 1.91; N, 4.09. Found: C, 26.50; H, 1.79; N, 4.24.



Terminal Oxidants

General procedure for testing the oxidants: 50 mg of substrate, appropriate amount of terminal oxidant and catalyst were added to 5 mL DCM. The reaction was stirred under nitrogen for 3h (in the case of epoxidation) or 6h (in the case of C–H oxidation) unless stated otherwise. ¹HNMR analysis was performed after solvent removal unless stated otherwise. Results are organized by terminal oxidant and shown below.

Tetra(n-butyl)ammonium oxone*

Trans-stilbene epoxidation

Catalyst	Loading	Oxidant eq	Time	Trans-epoxide	Cis-epoxide
1	2%	3	5 hr	21%	0
/	0%	3	5 hr	1%	0

*Excess tetra(n-butyl)ammonium oxone was removed by water washing (5x)

mCPBA*

Ethylbenzene C–H oxidation

Catalyst	Loading	Oxidant eq	Solvent	Time	Yield
1	5%	4	1:1 tBuOH/H ₂ O	12hrs	0%

*Excess acid was removed by saturated sodium bicarbonate solution washing

Iodosobenzene Diacetate

Trans-stilbene epoxidation

Catalyst	Loading	Oxidant eq	Trans-epoxide	Cis-epoxide	Iodosobenzene Diacetate consumption
none	0%	2	1%	0	4%
1	3%	2	18%	0	100%
1	3%	10	15%	0	30%

N-Oxides

Trans-stilbene epoxidation

Catalyst	Loading	Oxidant	Oxidant eq	Time	trans-epoxide
1	2%	2,6-Dichloropyridine N-oxide	2	5hrs	trace
none	0%	2,6-Dichloropyridine N-oxide	2	5hrs	trace

trimethylamine oxide, pyridine N-oxide, picolin N-oxide, N-Methylmorpholine-N-Oxide, no color change

2,6-Dimethylpyridine N-oxide, trace amount of product

(2,6-Dichloropyridine N-oxide) MeCN solvent, no effect on heating

Iodosobenzene^{vii}

Trans-stilbene epoxidation

Catalyst	Loading	Oxidant eq	Trans-epoxide	Cis-epoxide	Iodosobenzene consumption
none	0%	3	0%	0%	1%
1	2%	3	4%	0%	17%
1	2%	3	6%	0%	18%
1	2%	10	6%	0%	4%

Cis-stilbene epoxidation

Catalyst	Loading	Oxidant eq	Trans-epoxide	Cis-epoxide	Iodosobenzene consumption
1	2%	3	1%	3%	18%
1	2%	3	1%	1%	12%
none	0%	3	0%	0%	5%

Solvents

Solvents were tested by following the general procedure for C–H oxidation in the paper. Yields are shown below.

Entry	Solvent	Ethylbenzene Oxidation	Cis-decalin Oxidation
1	tBuOH/H ₂ O 1:1	55%	25%
2	tBuOH/pH2 Aq Buffer 1:1		20%
3	tBuOH&100uL H ₂ O		<1%
5	H ₂ O	21%	
6	AcOH/H ₂ O 1:1	18%	0%
7	Acetone	substrate not soluble	
8	Formic Acid		0%
9	DCM/H ₂ O with Na(BPh) ₄	0%	
10	1:1 N-Methyl-2-pyrrolidone/H ₂ O		0%
11	EtOH/H ₂ O 2:1	0.3%	
12	*DMSO 1:1	0%	
13	*DMF 1:1	0%	
14	HFIP/H ₂ O 1:1		substrate not soluble
15	^a tBuCOOH/H ₂ O 1:1		<1%
16	tBuOH/H ₂ O 9:1		6%

HFIP = (CF₃)₂CHOH

^aAt 40°

References

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