

Mechanism of Efficient Anti-Markovnikov Olefin Hydroarylation Catalyzed by Homogeneous Ir(III) Complexes

Gaurav Bhalla,^a Steven M. Bischof,^b Somesh K. Ganesh,^{a,b} Xiang Yang Liu,^a CJ Jones,^a Andrey Borzenko,^a William J. Tenn, III,^a Daniel H. Ess,^{b,c} Brian G. Hashiguchi,^b Kapil S. Lokare,^b Chin Hin Leung,^b Jonas Oxgaard,^c William A. Goddard, III,^{c,*} and Roy A. Periana^{a,b,*}

^a The Loker Hydrocarbon Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089

^b The Scripps Energy Laboratories, Department of Chemistry, The Scripps Research Institute, Jupiter, Florida 33458

^c Materials and Process Simulation Center, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Warning! Organomercury compounds are highly toxic! There is a danger of cumulative effects. These compounds may cause serious and irreversible effects on skin contact. These compounds may be fatal if absorbed through the skin - even small amounts, such as a single drop, may cause serious injury or potentially be fatal. They may cause metal fume fever if inhaled or swallowed. Chronic exposure may cause irreversible CNS damage, sensitization, weight loss, immunological disease and other serious effects. Work with these dangerously toxic compounds must not begin before a full assessment of the risks has been made and suitable protocols established including reading and understanding available safety information (MSDS).

Experimental Conditions. All manipulations were carried out using glovebox and high vacuum line techniques under an inert atmosphere of N₂ or argon. Benzene, benzene-d₆, toluene-d₈ and THF were purified by vacuum transfer from sodium benzophenone ketyl. CD₂Cl₂ and pyridine were dried by vacuum transfer from CaH₂. Synthetic work involving iridium complexes was carried out in an inert atmosphere in spite of the air stability of the complexes. Reagent-grade chemicals and solvents were used as is and purchased from Aldrich or Strem. CH₃¹³CH₂I was purchased from Cambridge Isotopes Inc. and was used as received. Complexes **R-Ir-L**, [**R-Ir**]₂ and **cis R-Ir-L**,**Error! Bookmark not defined.**ⁱ and diethylmercuryⁱⁱ were prepared as described in the literature. Elemental analyses were done by Desert Analytics laboratory; Tucson, Arizona. Liquid phases of the reaction mixtures were analyzed with a Shimadzu GC-MS QP5000 (ver. 2) equipped with cross-linked methyl silicone gum capillary column, DB5. Gas measurements were performed using a GasPro column. The retention times of the products were confirmed by comparison to authentic samples. NMR spectra were obtained on a Bruker AM-360 (360.138 MHz for ¹H and 90.566 MHz for ¹³C), Bruker AC-250 (250.134 MHz for ¹H and 62.902 MHz for ¹³C) or on a Varian Mercury 400 (400.151 MHz for ¹H and 100.631 MHz for ¹³C) spectrometer. Chemical shifts are given in ppm relative to TMS or to residual solvent proton resonances. All carbon resonances are singlets unless otherwise mentioned.

Table S1. Kinetic dependence of hydroarylation on benzene concentration

Benz / [M]	TN
2.8	1.05
5.6	2.445
8.4	3.3
11.2	5.2

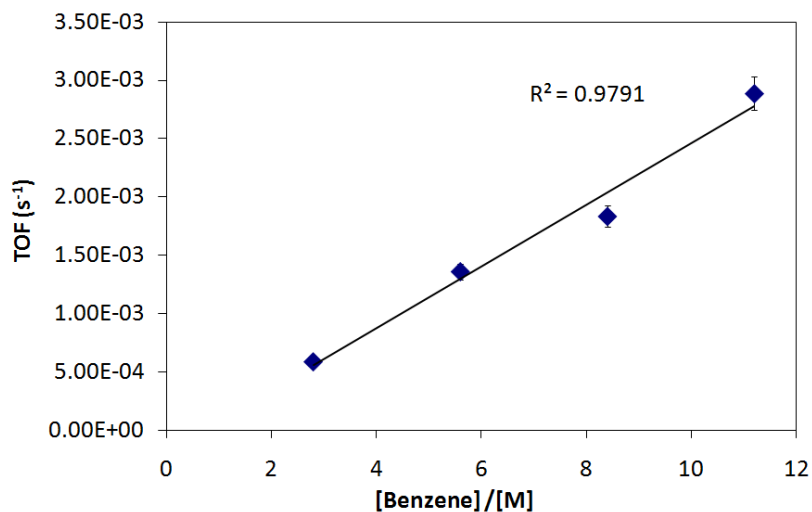


Table S2. Kinetic dependence of hydroarylation on olefin concentration

Styr / [M]	TN
1.454633	1.36
2.493656	2.76
3.272924	5.24
3.879021	2.56
4.363898	1.42

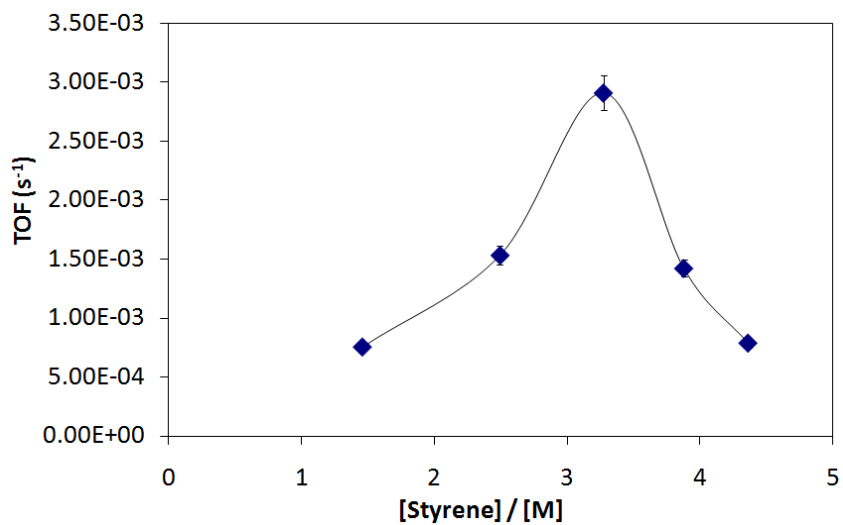


Table S3. Kinetic Dependence of Hydroarylation on Pyridine Concentration

1/Py Eq.	TN
0.37	1.63
0.185	0.81
0.123	0.57
0.093	0.49

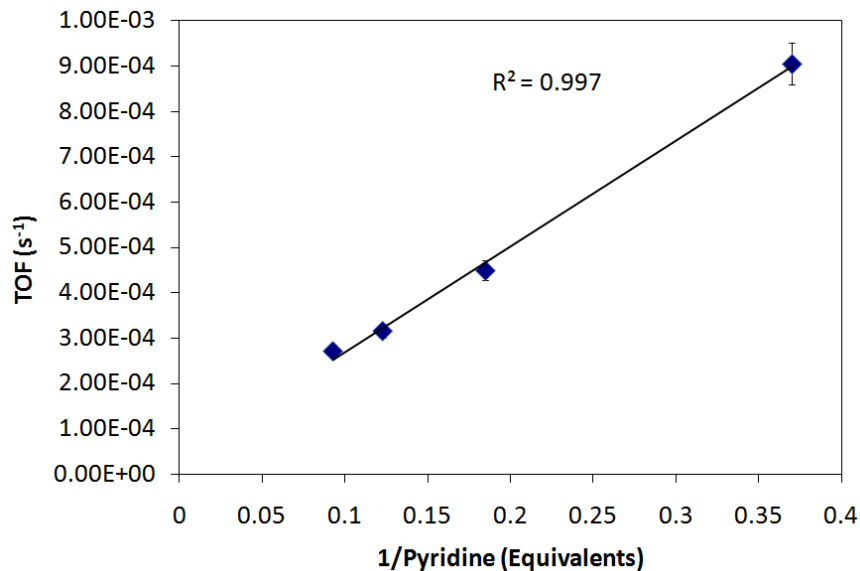


Table S4. TON at various Time (s) for Ph-Ir-Py.

Time (s)	TN
1800	1.9
7200	9.0
14400	19.3

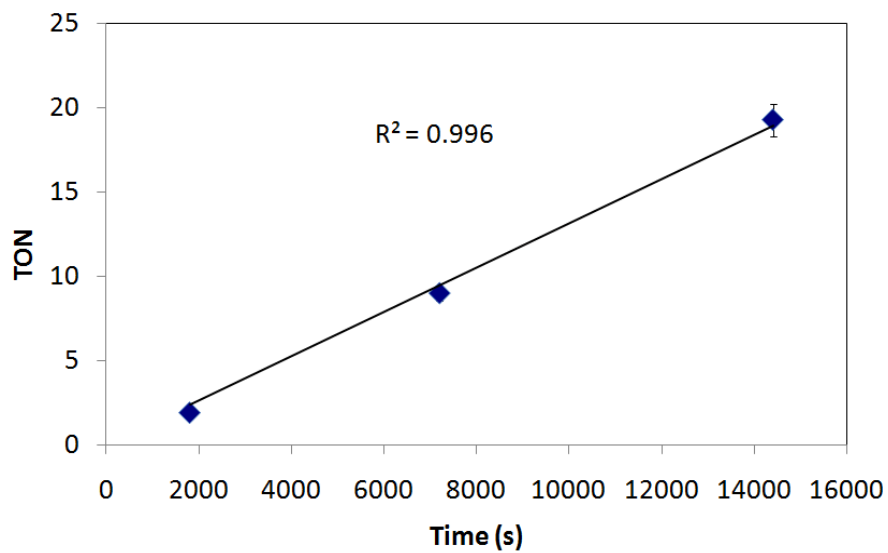


Table S5. Rate difference between Ph-Ir-Py Vs Ph-Ir-H₂O

Time / h	TN (H ₂ O)	TN (Py)
0	0	0
0.25	14.11	2.3
0.5	14.62	5.21
1	15.13	5.33
1.5	15.3	5.41
2	15.3	5.55

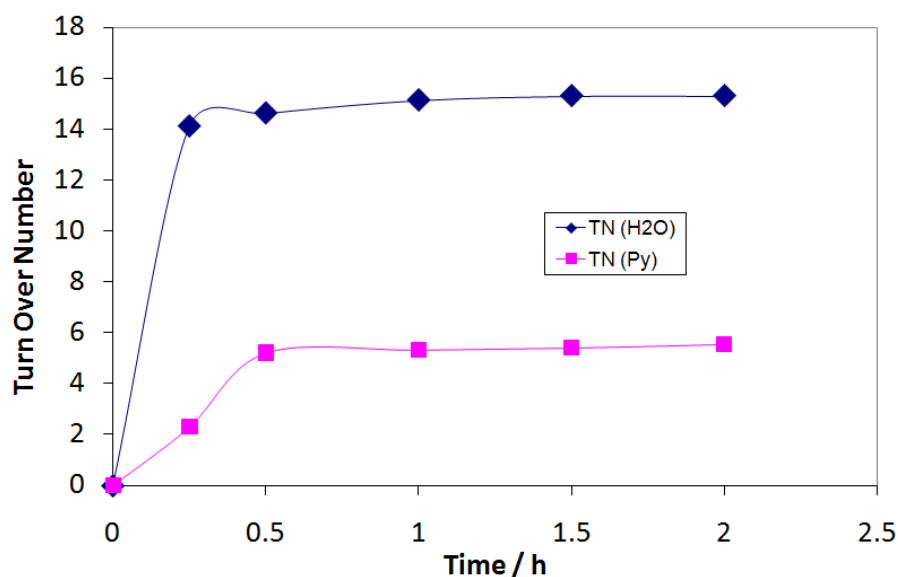


Table S6. Comparison of thermodynamic and experimental ratio for hydroarylation with various olefins.

olefin	-	B3LYP-G	B3LYP-G	dG kcal/mol	exptal	DFT ratio
-	-	A(linear)	B(branched)	-	-	-
propylene	C ₉ H ₁₂	-350.13573	-350.134	0.9	61:39	74:36
styrene	C ₁₄ H ₁₄	-541.87036	-541.865	3.2	98:2	97: 03
1-hexene	C ₁₂ H ₁₈	-468.02955	-468.027	1.9	69:31	87: 13
isobutylene	C ₁₀ H ₁₄	-389.43316	-389.428	2.9	82:18	96:4

B3LYP-G values are B3LYP/LACV3P++**//LACVP** gas phase values.

ⁱ Bennett, M. A.; Mitchell, T. R. B. *Inorg. Chem.* **1976**, 15, 2936.

ⁱⁱ Gilman, H., and Brown, R. E., *J. Am. Chem. Soc.* **1929**, 51, 928.