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Mechanistic Insights Into Iridium-Catalyzed Asymmetric Hydrogenations of Dienes

Xiuhua Cui, Yubo Fan, Michael B. Hall* and Kevin Burgess*

Department of Chemistry, Texas A & M University, P.O. Box 30012, College Station, Texas 77842.

burgess@tamu.edu

- full reference 32
- synthesis of **2**, **4** and **5** for authentic samples and/or assignments of absolute configurations
- kinetic experiments
- NMR experiments
- catalyst screening
- coordinates from the DFT calculations

Reference 32: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuki, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Stefano, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanyakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Willingford, CT, 2004, p Gaussian 03, Revision B.05.

General Procedures

NMR spectra were recorded on a Varian Unity Plus 300 spectrometer (^1H at 300 MHz, and ^{13}C at 75 MHz). Chemical shifts of ^1H and ^{13}C spectra were referenced to the NMR solvents. Optical rotations were measured on Jasco DIP-360 digital polarimeter. Flash chromatography was performed using silica gel (230–600 mesh). Thin layer chromatography was performed using glass plates coated with silica gel 60 F254 (E. Merck, Darmstadt, Germany). Toluene and THF were distilled over Na/benzophenone. Dichloromethane and acetonitrile were dried over CaH_2 . Racemic and optically active 1,2-diphenylpropan-1-one, iridium catalyst **C** were prepared using literature methods.^{1,2} 2,3-Diphenylbutadiene was purchased from Fluka and purified by flash chromatography using hexanes as the eluent before use. Other solvents and reagents were used as received. The hydrogenation results were analyzed using GC with a chiral column³ [carrier gas: helium; temperature: 120 °C; flow rate: 2.0 ml/min; retention time (min): 37.5 (**3**), 38.9 (*ent*-**3**), 41.3 (**4**), 49.7 (*meso*-**3**), 51.0 (**2**), 53.3 (*ent*-**2**), 54.1 (*cis*-**4**), 63.1 (**1**)].

Synthesis of 2, 4 and 5 for Authentic Samples and/or Assignments of Absolute Configurations

Preparation of Racemic 2,3-Diphenylbut-1-ene 2. A mixture of racemic 2,3-diphenylpropan-1-one (1.83 g, 8.7 mmol), methyl triphenylphosphonium bromide (1.07 g, 9.6 mmol), and KO^tBu (3.41 g, 9.6 mmol) in 70 mL anhydrous THF was stirred at ambient temperature for 20 h. The solvent was evaporated under reduced pressure and the product was extracted with *n*-pentane (50 mL × 3). The pure product (1.44 g, 80 %) was obtained as a colorless oil after flash chromatography using hexanes as the eluent. ¹H NMR δ (ppm): 7.34 - 7.14 (m, 10H), 5.44 (m, 1H), 5.18 (m, 1H), 4.05 (q, 1H, J = 6.9 Hz), 1.49 (dd, 3H, J = 0.9, 6.9 Hz). ¹³C NMR δ (ppm): 152.56, 145.01, 142.17, 128.31, 127.61, 127.09, 126.68, 126.03, 113.03, 112.95, 44.11, 21.66.

Preparation of Optical Active 2,3-Diphenylbut-1-ene. A mixture of methyl triphenylphosphonium bromide (137 mg, 0.384 mmol) and KO^tBu (43 mg, 0.384 mmol) in 3 mL of anhydrous THF was stirred at ambient temperature for 4 h, and then transferred to a THF (1 mL) solution of (-)-(R)-2,3-diphenylpropan-1-one⁴ (50% *ee*, 80 mg, 0.384 mmol). The solution was stirred for 1 h, then H₂O (10 mL) was added. The product was extracted with hexanes (20 mL × 3), dried over MgSO₄, and purified by flash chromatography using hexanes as the eluent. The pure product, (-)-(R)-2,3-diphenylbut-1-ene (47% *ee*, 72 mg, 89 %), was obtained as a colorless oil.

Preparation of Racemic 2-Phenyl-3-(4-methylphenyl)but-1-ene 5. A THF (35 mL) solution of 1-phenyl-2-(4-methylphenyl)-propan-1-one (774 mg, 3.5 mmol), methyl triphenylphosphonium bromide (1.23 g, 3.5 mmol), and KO^tBu (387 mg, 3.5 mmol) was stirred at ambient temperature for 16 h, then H₂O (20 mL) was added. The reaction mixture was subjected to aqueous extraction and chromatography as described above for 2,3-diphenylbut-1-ene. The pure product (342 mg, 45%) was obtained as a colorless oil. ¹H NMR δ (ppm): 7.41 - 7.13 (m, 9H), 5.49 (m, 1H), 5.24 (m, 1H), 4.08 (q, 1H, J = 7.2 Hz), 2.37 (s, 3H), 1.54 (d, 3H, J = 7.2 Hz). ¹³C NMR δ (ppm): 152.72, 142.26, 142.01, 129.03, 128.00, 127.46, 127.05, 126.66, 112.81, 43.68, 21.78, 20.97.

Preparation of *cis* and *trans*-2,3-Diphenylbut-2-ene 4. The title compounds were prepared using a literature procedure featuring the McMurry reaction.⁵ The *cis* and *trans* products were obtained in a ratio of 1.2:1.0 as determined by both ¹H NMR and GC. Retention time for *cis* isomer: 41.3 min, and *trans* isomer: 54.1 min.

Kinetic Experiments

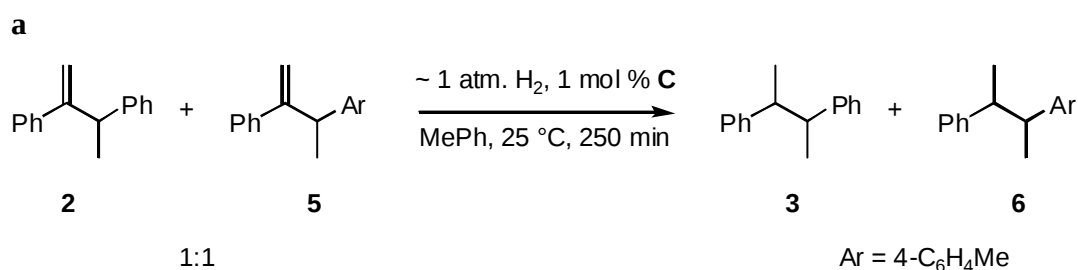
Solvent Effects for the Kinetic Experiments. This experiment was done in three test tubes of approximately $1.0 \times 10 \text{ cm}^2$ in a Parr bomb. 2,3-Diphenylbutadiene **1** (20.6 mg, 0.1 mmol) and Ir catalyst **C** were added to each tube. CH_2Cl_2 , CHCl_3 , and toluene (0.1 mL for all three) were chosen as the tested solvents. The bomb was flushed with H_2 for 20 min without stirring. The reactions were then stirred at ambient temperature, $\sim 1 \text{ atm}$ H_2 pressure, and 500 rpm for 18 hours. The solution was then passed through a silica plug using hexanes:EtOAc = 3:7 (v:v) as the eluent to remove the catalyst. The yields and enantiomeric excess were then analyzed by GC, and the results are summarized in **S-Table 1**. Similar reactivity and selectivity were obtained using CH_2Cl_2 , CHCl_3 , or toluene. Toluene was chosen as the solvent for the following kinetic studies purely because its high boiling point and low volatility are suitable for the length of the necessary reaction time.

S-Table 1. Hydrogenation of 2,3-diphenyl butadiene with different solvents

solvent	conversion	<i>ee</i> of 3	<i>rac 3</i> : <i>meso 3</i>
	(%)	(%)	
CH_2Cl_2	> 99	87	27:73
CHCl_3	> 99	90	30:70
toluene	> 99	87	28:72

Typical Hydrogenation Procedure for Kinetic Experiment at 1 Atm Pressure. A 25 mL two neck pear-shaped flask was connected to a bubbler and to a hydrogen tank through a valve to control the pressure. 2,3-Diphenylbutadiene (412.6 mg, 2 mmol) and the Ir catalyst **C** (32.5 mg, 0.02 mmol) were added and the flask was then flushed with hydrogen for 30 min at a controlled water bath temperature of $25.0 \pm 0.1 \text{ }^\circ\text{C}$. The pressure was adjusted to 1 atm, then toluene (2.0 mL) was added via a syringe. The reaction was stirred at $25.0 \pm 0.1 \text{ }^\circ\text{C}$, 500 rpm and 1 atm hydrogen pressure until a precipitate was formed (approximately 10 h). An aliquot of 0.05 mL solution was taken via a syringe every 5 to 40 min, passed through a silica plug with hexanes:EtOAc = 3:7 (v:v) as the eluent. The product ratios, yields, and enantiomeric excesses were determined using GC, and the results are summarized in **Figure 1** in text.

Hydrogenation of the Mixture of Racemic 2,3-Diphenylbut-1-ene **2 and Racemic 2-Phenyl-3-(4-methylphenyl)but-1-ene **5** to Compare Their Relative Reactivity.** The typical hydrogenation procedure for kinetic experiments at 1 atm H_2 pressure was followed

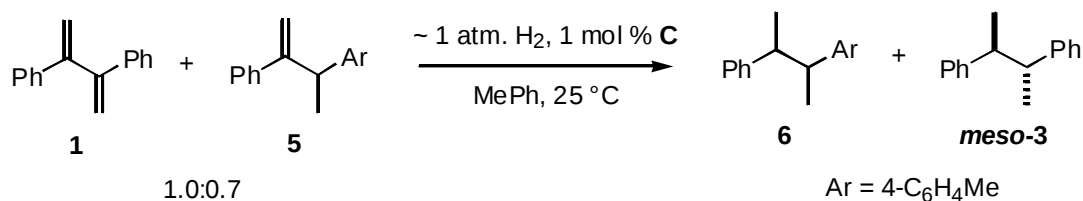


Time (min)	3 (mol/L)	6 (mol/L)
60	0.18	0.21
90	0.26	0.30
120	0.33	0.36
150	0.39	0.42
186	0.45	0.47
226	0.50	0.50

S-Figure 1. a The reaction for relative reactivity comparison; and **b** GC results for reaction shown

Hydrogenation of 2,3-Diphenyl-butadiene 1 and 2-Phenyl-3-(4-methylphenyl)but-1-ene 5: A Competition Experiment to Prove Dissociation of the Substrate From the Metal. The general procedure for kinetic experiments at 1 atm H₂ pressure was followed using 2,3-diphenylbutadiene **1** (144.4 mg, 0.7 mmol), Ir catalyst **C** (11.4 mg, 0.007 mmol), and toluene (0.7 mL) for 55 min. 2-Phenyl-3-(4-methylphenyl)but-1-ene **5** (105.0 mg, 0.47 mmol) was added via a syringe, and H₂ was then bubbled through instead of being controlled at exactly 1 atm. The pressure was not monitored closely to make them constant throughout the experiment (Constant pressure is not necessary in this experiment). An aliquot of 0.05 mL

solution was taken at 30, 150, 240, and 300 min respectively after **5** was introduced. The reaction and GC analysis are summarized in **S-Figure 2**.



time (min)	<i>meso</i> - 3 (mol/L)	6 (mol/L)
30	0.012	0
150	0.059	0.004
240	0.089	0.011
300	0.13	0.018

S-Figure 2. a The reaction for competitive experiment, and **b** GC results for reaction shown in **a**.

Hydrogen Diffusion Effects. The general procedure for kinetic experiments at 1 atm H_2 pressure was followed to study hydrogen diffusion effects.

For [catalyst] = 0.0075 mol/L, 2,3-diphenylbutadiene (206.3 mg, 1.0 mmol), Ir catalyst **C** (12.2 mg, 0.0075 mmol), and toluene (1.0 mL) were used.

For [catalyst] = 0.01 mol/L, 2,3-diphenylbutadiene (154.7 mg, 0.75 mmol), Ir catalyst **C** (12.2 mg, 0.0075 mmol), and toluene (0.75 mL) were used.

For [catalyst] = 0.015 mol/L, 2,3-diphenylbutadiene (123.8 mg, 0.60 mmol), Ir catalyst **C** (14.6 mg, 0.0090 mmol), and toluene (0.60 mL) were used.

For the control experiment summarized in **Table 2** in the text, the reaction was carried out in a schlenk tube of ~ 2.5 cm diameter. For entry 2 in Table 2, the maximum stir speed of the IKA[®]

WERKE RET basic magnetic stirred was used.

Dependence on Catalyst Concentration. The general procedure for kinetic experiments at 1 atm H₂ pressure was followed. Each experiment was repeated twice at 700 rpm stir speed.

For [catalyst] = 0.01 mol/L, 2,3-diphenylbutadiene (154.7 mg, 0.75 mmol), Ir catalyst **C** (12.2 mg, 0.0075 mmol), and toluene (0.75 mL) were used.

For [catalyst] = 0.0075 mol/L, 2,3-diphenylbutadiene (206.3 mg, 1.0 mmol), Ir catalyst **C** (12.2 mg, 0.0075 mmol), and toluene (1.0 mL) were used.

For [catalyst] = 0.0060 mol/L, 2,3-diphenylbutadiene (165.0 mg, 0.80 mmol), Ir catalyst **C** (7.8 mg, 0.0048 mmol), and toluene (0.80 mL) were used.

For [catalyst] = 0.0050 mol/L, 2,3-diphenylbutadiene (206.3 mg, 1.0 mmol), Ir catalyst **C** (8.1 mg, 0.0050 mmol), and toluene (1.0 mL) were used.

For [catalyst] = 0.0040 mol/L, 2,3-diphenylbutadiene (206.3 mg, 1.0 mmol), Ir catalyst **C** (6.5 mg, 0.0040 mmol), and toluene (1.0 mL) were used.

For [catalyst] = 0.0030 mol/L, 2,3-diphenylbutadiene (206.3 mg, 1.0 mmol), Ir catalyst **C** (4.9 mg, 0.0030 mmol), and toluene (1.0 mL) were used.

Typical results of diene conversion with time at each catalyst concentration, reaction rate, *ie* $-[\text{diene}]/dt$, at each catalyst concentration, and dependence of reaction rate on catalyst concentration are summarized in **S-Table 2**.

S-Table 2. Dependence of Reaction Rate on Catalyst Concentration.

a. [catalyst] = 0.0030 mol/L.

Time (min)	[diene] (mol/L)	
	1 st exp.	2 nd exp.
30	0.96	0.97
60	0.94	0.95
90	0.92	0.93
120	0.90	0.90
150	0.88	0.88
180	0.86	0.86
-[diene]/dt (10 ⁻³ mol/L/min)	0.72	0.75
R ²	1.0	1.0

b. [catalyst] = 0.0040 mol/L.

Time (min)	[diene] (mol/L)	
	1 st exp.	2 nd exp.
30	0.97	0.97
60	0.94	0.93
90	0.90	0.90
120	0.87	0.87
150	0.84	0.83
180	0.80	0.80
-[diene]/dt (10 ⁻³ mol/L/min)	1.1	1.1
R ²	1.0	1.0

continued from S-Table 2

c. [catalyst] = 0.0050 mol/L.

Time (min)	[diene] (mol/L)	
	1 st exp.	2 nd exp.
20	0.97	0.96
40	0.94	0.93
60	0.92	0.90
80	0.89	0.87
100	0.86	0.84
120	0.84	0.81
-[diene]/dt (10^{-3} mol/L/min)	1.3	1.5
R ²	1.0	1.0

d. [catalyst] = 0.0060 mol/L.

Time (min)	[diene] (mol/L)	
	1 st exp.	2 nd exp.
30	0.95	0.96
60	0.90	0.91
90	0.86	0.86
120	0.81	0.82
150	0.76	0.77
180	0.71	0.72
-[diene]/dt (10^{-3} mol/L/min)	1.6	1.6
R ²	1.0	1.0

e. [catalyst] = 0.0075 mol/L.

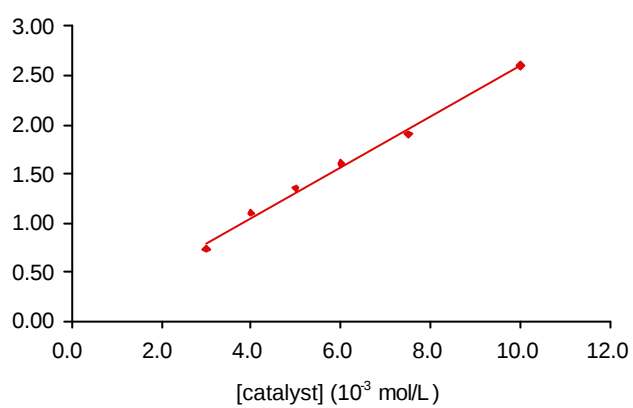
Time (min)	[diene] (mol/L)	
	1 st exp.	2 nd exp.
20	-	0.96
40	0.93	0.93
60	0.89	0.89
80	0.85	0.85
100	0.82	0.82
120	0.78	0.78
150	0.72	-
-[diene]/dt (10^{-3} mol/L/min)	1.9	1.9
R ²	1.0	1.0

f. [catalyst] = 0.010 mol/L.

Time (min)	[diene] (mol/L)	
	1 st exp.	2 nd exp.
20	0.97	0.97
40	0.92	0.92
60	0.87	0.87
80	0.81	0.82
100	0.76	0.77
120	0.71	0.71
150	0.63	-
-[diene]/dt (10^{-3} mol/L/min)	2.6	2.6
R ²	1.0	1.0

*continued from S-Table 2***g.** Dependence of reaction rate on catalyst concentration.

[cat] (mol/L)	0.0030	0.0040	0.0050	0.0060	0.0075	0.010
-[diene]/dt	0.72	1.1	1.3	1.6	1.9	2.6
(10 ⁻³ mol/L)	0.75	1.1	1.4	1.6	1.9	2.6
average	0.75	1.1	1.35	1.6	1.9	2.6
d(-d[diene]/dt)/d[cat]	0.26					
(min ⁻¹)						
R ²	0.99					



Dependence on Hydrogen Pressure. 2,3-Diphenylbutadiene **1** (206.3 mg, 1.0 mmol) and Ir catalyst **C** (12.2 mg, 0.0075 mmol) were transferred to a 10 mL pear shape flask, which was then flushed with N₂ for 20 min. Toluene (1 mL) was added to prepare the stock solution. For experiments at elevated pressure, 0.1 mL stock solution was transferred to a test tube of approximately 1.0 x 10 cm². The bomb was flushed with hydrogen for 2 min without stirring, and the pressure was then increased to the desired value. The solution was stirred at maximum speed for the designated time before the bomb was vented. A routine work up and analysis procedure were followed as described in typical hydrogenation procedure for kinetic experiments at 1 atm H₂ pressure. The reaction time, conversion of diene **1** with time, reaction rate-H₂ pressure linear relationship are summarized in **S-Table 3**.

S-Table 3. Dependence of Reaction Rate on Hydrogen Pressure.

a. P(H₂) = 1.0 atm.

time (min)	[diene] (mol/L)	
	1 st exp.	2 nd exp.
20	0.95	0.94
40	0.90	0.88
60	0.85	0.83
81	0.80	0.77
95	0.75	-
100	-	0.72
120	0.69	0.66
162	0.57	0.56
-d[diene]/dt (10 ⁻³ mol/L/min)	2.7	2.7
R ²	1.0	1.0

Continued from S-Table 3

b. $P(\text{H}_2) = 4.9 \text{ atm.}$

time (min)	[diene] (mol/L)			
	1 st exp.	2 nd exp.	3 rd exp.	4 th exp.
0	1	1	1	1
3	0.90	0.90	0.90	-
6	0.83	0.83	0.86	-
9	0.75	0.77	0.81	-
12	0.71	0.70	0.73	-
15	0.63	0.66	0.67	0.57
18	0.59	0.55	-	-
5	-	-	-	0.84
10	-	-	-	0.72
20	-	-	-	0.48
25	-	-	-	0.30
30	-	-	-	0.14
$-\text{d}[\text{diene}]/\text{dt}$ ($10^{-2} \text{ mol/L/min}$)	2.2	2.3	2.1	2.8
R^2	0.99	0.99	0.99	1.0

c. $P(\text{H}_2) = 6.8 \text{ atm.}$

time (min)	[diene] (mol/L)			
	1 st exp.	2 nd exp.	3 rd exp.	4 th exp.
0	1.0	1.0	1.0	1.0
3	-	0.90	0.86	0.88
6	-	0.83	0.76	0.80
9	-	0.77	0.68	0.69
12	-	0.70	0.61	0.60
15	0.53	0.62	0.52	0.46
18	-	0.55	0.47	0.45
5	0.81	-	-	-
10	0.66	-	-	-
20	0.38	-	-	-
25	0.23	-	-	-
30	0.14	-	-	-
$-\text{d}[\text{diene}]/\text{dt}$ ($10^{-2} \text{ mol/L/min}$)	2.9	2.4	2.9	3.2
R^2	1.0	1.0	0.98	0.98

Continued from *S-Table 3***d.** $P(\text{H}_2) = 8.2 \text{ atm.}$

Time (min)	[diene] (mol/L)			
	1 st exp.	2 nd exp.	3 rd exp.	4 th exp.
0	1.0	1.0	1.0	1.0
3	0.86	0.86	0.87	0.86
6	0.74	0.77	0.73	0.72
9	0.64	0.67	0.68	0.60
12	0.50	0.54	0.59	0.44
15	0.39	0.49	0.42	0.29
18	-	-	0.29	0.19
20	0.22			
-d[diene]/dt ($10^{-2} \text{ mol/L/min}$)	3.9	3.5	3.8	4.6
R^2	1.0	1.0	0.99	1.0

e. $P(\text{H}_2) = 9.9 \text{ atm.}$

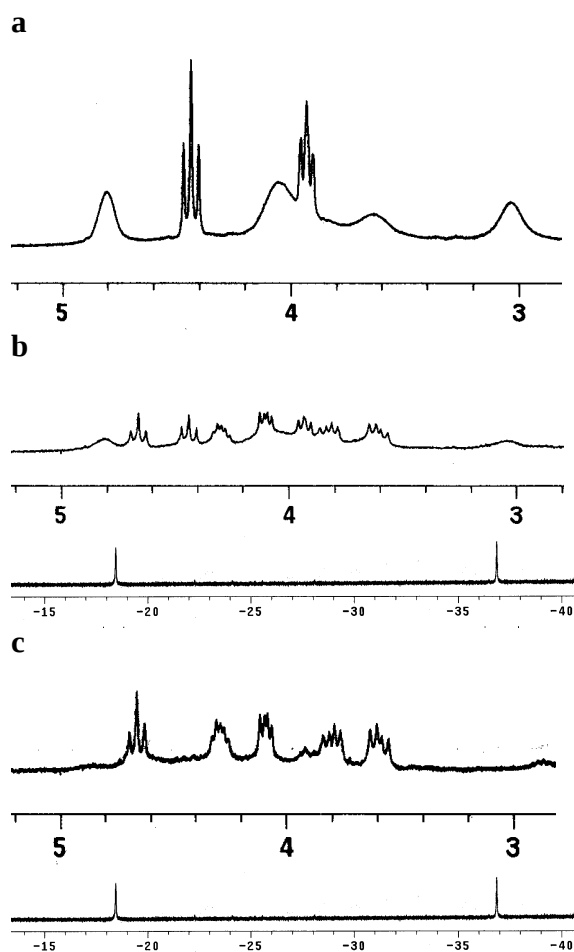
time (min)	[diene] (mol/L)			
	1 st exp.	2 nd exp.	3 rd exp.	4 th exp.
3	0.85	0.80	0.82	0.81
6	0.77	0.64	0.70	0.66
9	-	0.51	0.59	-
12	0.56	0.33	0.51	0.40
15	0.48	-	0.35	0.23
18	-	-	-	0.07
20	0.23	-	-	-
-d[diene]/dt ($10^{-2} \text{ mol/L/min}$)	3.7	5.2	3.8	4.8
R^2	0.99	1.0	0.99	1.0

Continued from *S-Table3*f. Reaction rate- H_2 pressure linear relationship.

P(H_2) (atm)		1.0	4.9	6.8	8.2	9.9
-d[diene]/dt (10^{-3} mol/L/min)	1	0.27	2.2	2.9	3.9	3.7
	2	0.27	2.3	2.4	3.5	5.2
	3	-	2.1	2.9	3.8	3.8
	4	-	2.8	3.2	4.6	4.8
	average	0.27	2.4	2.9	4.0	4.4
d(-d[diene]/dt)/d(P(H_2)) (10^{-3} mol/L/min/atm)		4.7				

NMR Experiments

Hydrogenation of Ir Catalyst C in CDCl_3 . Ir catalyst **C** (16.2 mg, 0.01 mmol) was transferred to an NMR tube. CDCl_3 (0.5 mL) was added. The tube was filled with N_2 by three freeze-thaw cycles. Hydrogen was then bubbled through for 20 min. The typical regions of the ^1H NMR are shown in **S-Figure 3b**. The same experiment was repeated with 40 min reaction time, and the ^1H NMR are shown in **S-Figure 3c**. When longer reaction time was used, no obvious changes were observed in ^1H NMR spectrum.



S-Figure 3. Hydrogenation in CDCl_3 with **a** ^1H NMR signals of a pure catalyst **C**; **b** catalyst **C** hydrogenated at ~ 1 atm for 20 min; and, **c** catalyst **C** hydrogenated at ~ 1 atm for 40 min.

Hydrogenation of Diene 1 with “Hydrogenated Catalyst” in CDCl_3 . The Ir catalyst **C** (16.2 mg, 0.01 mmol) in CDCl_3 (0.5 mL) was bubbled with H_2 for 60 min. Diene **1** (10.3 mg, 0.05 mmol) dissolved in CDCl_3 (0.5 mL) was added via a syringe. The solution was bubbled with H_2 for 30 min. No alkanes **3** or partially hydrogenated intermediates **2** are observed by ^1H NMR.

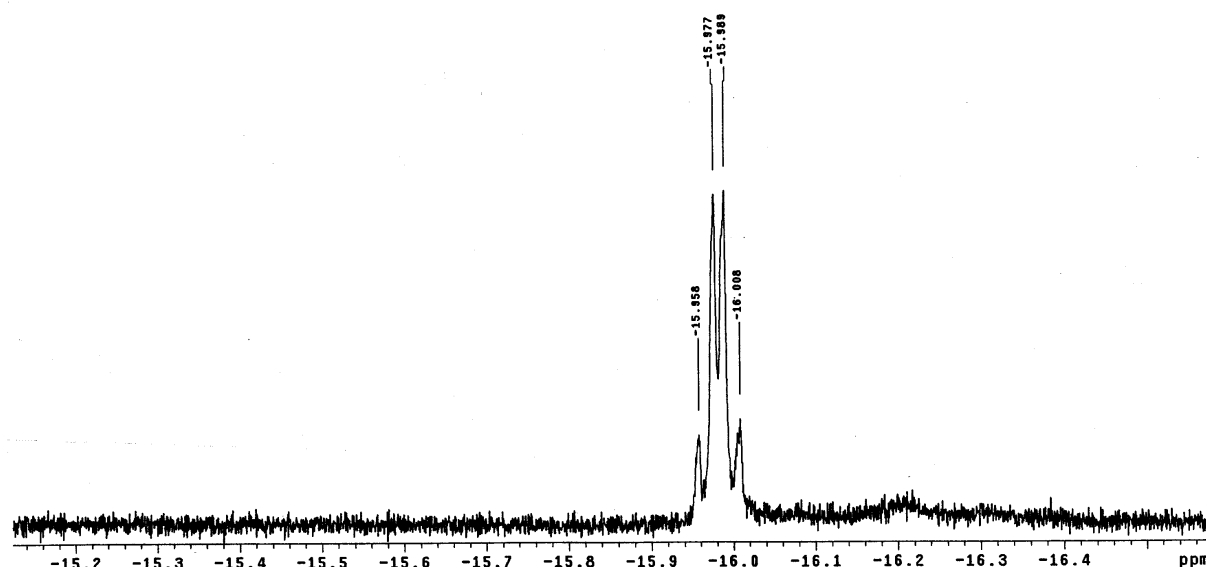
Hydrogenation of Ir Catalyst C in Toluene- d^8 . Ir catalyst **C** (16.2 mg, 0.01 mmol) was transferred to an NMR tube. Toluene- d^8 (0.5 mL) was added. The tube was filled with N_2 by three

freeze-thaw cycles. Hydrogen was then bubbled through for 1h or 5h. The typical hydride regions of the ^1H NMR are shown in **S-Figure 4a**.

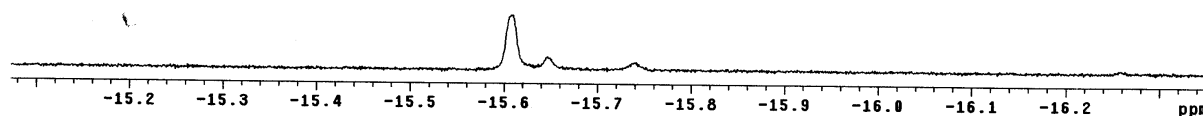
Hydrogenation of Diene 1 with Ir Catalyst C in Toluene- d^8 . Ir catalyst **C** (16.2 mg, 0.01 mmol), and diene **1** (10.3 mg, 0.05 mmol) were transferred to an NMR tube. Toluene- d^8 (0.5 mL) was added. The tube was filled with N_2 by three freeze-thaw cycles. Hydrogen was then bubbled through for 20 min. The typical hydride regions of the ^1H NMR are shown in **S-Figure 4b**.

Hydrogenation of Diene 1 with “Hydrogenated Catalyst” in Toluene- d^8 . The Ir catalyst **C** (10.0 mg, 0.006 mmol) was transferred to an NMR tube. Toluene- d^8 (0.5 mL) was added. The tube was filled with N_2 by three freeze-thaw cycles. Hydrogen was then bubbled through for 1h. Diene **1** (64 mg, 0.308 mmol) dissolved in Toluene- d^8 (0.5 mL) was added via a syringe after degas by three freeze-thaw cycles. The solution was bubbled with H_2 for 12 min. The product distribution is shown in **S-Figure 4c**.

a



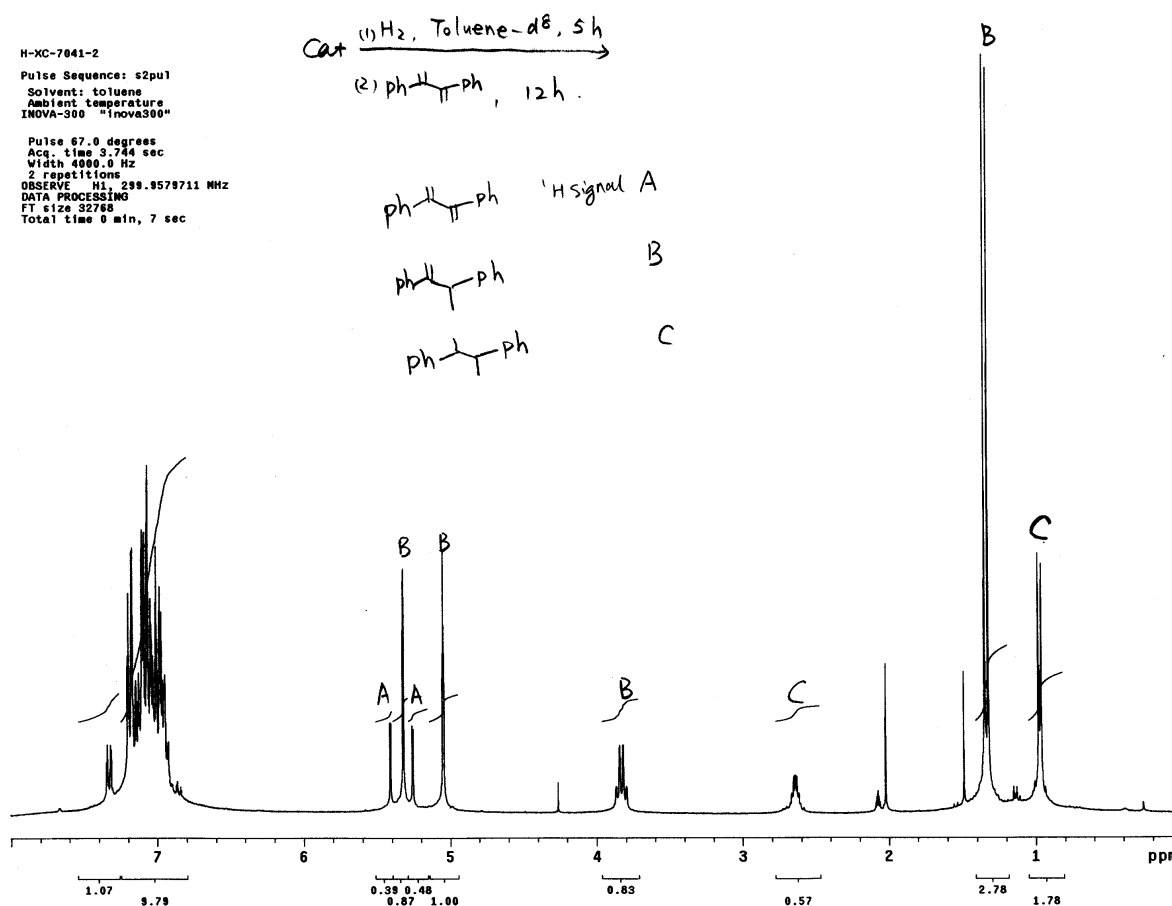
b



S-Figure 4. ^1H NMR signals of **a** hydrogenated catalyst **C**; **b** hydrogenation of diene **1** with catalyst **C** at 1 atm for 20 min; and, **c** hydrogenation of diene **1** with ‘hydrogenated catalyst **C**’

S-Figure 4. continued

c



Catalyst Screening

Typical Procedure for Catalyst Screening. The hydrogenation was done in a test tube of approximately $1.0 \times 10 \text{ cm}^2$. Four tubes were screened in a Parr Bomb each time. 2,3-Diphenylbutadiene (20.6 mg, 0.1 mmol) and Ir catalyst C (0.001 mmol) were dissolved in toluene (0.1 mL). The bomb was flushed with hydrogen for 2 min without stirring before the pressure was increased to 10 bar. The reaction was stirred for 2 h at 500 rpm, and the bomb was then vented. The solvent was passed through a silica plug using hexanes/ethyl acetate (7/3, v/v) as the eluent. The hydrogenation results were obtained by GC analysis using a chiral column.

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- (2) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113-123.
- (3) Shitangkoon, A.; Vigh, G. *J. Chromatogr. A.* **1996**, *738*, 31-42.
- (4) Fox, J. M.; Huang, X.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360-1370.
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Energetics and Coordinates for the Complex Cations in Figure 7

Complex Cation P

E = -2128.45926095 A.U.
 E + ZPE = -2127.540530 A.U.
 E + H = -2127.491924 A.U.
 E + G = -2127.620577 A.U.

Ir	-0.317890	0.445065	0.217785
C	-1.196435	-0.548066	1.739964
N	-0.958223	-0.461319	3.110654
C	-1.786273	-1.339437	3.834546
C	-2.572973	-1.991460	2.914114
N	-2.214998	-1.506993	1.644482
N	1.754639	0.201509	1.108800
C	2.900101	-0.379931	0.772336
O	4.005115	0.025098	1.541247
C	3.549530	1.148922	2.410261
C	2.007626	1.029792	2.359121
C	1.414055	0.375148	3.627201
C	-0.110624	0.546307	3.782823
H	-1.753637	-1.417853	4.917477
H	-3.352608	-2.734443	3.046733
H	3.922619	2.088984	1.967553
H	3.987055	0.989907	3.408157
H	1.549703	2.019579	2.214386
H	1.876533	0.885131	4.496307
H	1.698010	-0.692446	3.690348
H	-0.372066	0.498647	4.854193
H	-0.411091	1.543591	3.410517
C	-2.979751	-1.884902	0.455359
C	-2.643100	-3.083828	-0.235351
C	-3.461656	-3.459768	-1.330137
C	-4.568834	-2.676059	-1.712863
C	-4.886115	-1.501177	-1.002175
C	-4.103267	-1.079858	0.101081
C	-1.479966	-3.984378	0.200705
C	-4.522215	0.164175	0.898020
C	-4.857281	1.373680	-0.015919
C	-5.732812	-0.169366	1.818472
C	-1.999591	-5.162786	1.075787
C	-0.675087	-4.537724	-1.004114
H	-3.233316	-4.375827	-1.885644
H	-5.191031	-2.986984	-2.560150
H	-5.755913	-0.906674	-1.303300
H	-3.680304	0.468326	1.549308
H	-0.786621	-3.380937	0.819686
H	-5.499041	-0.993374	2.517906
H	-6.019467	0.717078	2.415087
H	-6.610705	-0.474540	1.218667
H	-4.029070	1.602988	-0.711261
H	-5.762350	1.189152	-0.623610
H	-5.058712	2.269174	0.602315
H	-1.157404	-5.800877	1.403482
H	-2.527756	-4.805028	1.978328
H	-2.702811	-5.794034	0.500517
H	-0.374703	-3.728623	-1.693709
H	0.238523	-5.049389	-0.647444
H	-1.259703	-5.278885	-1.579903
C	3.311270	-1.407222	-0.271324
C	4.182586	-2.504846	0.451154
C	2.137237	-2.119909	-0.996377
C	4.219761	-0.686150	-1.337290
C	4.725680	-3.526082	-0.583030
C	2.688848	-3.145543	-2.028615
C	4.757873	-1.721185	-2.362232
C	5.611645	-2.788754	-1.625300
C	3.541104	-4.221818	-1.303957
C	3.566333	-2.411510	-3.079829
H	5.020507	-2.023438	0.985207

H	3.559415	-3.025615	1.206921
H	1.499002	-2.635614	-0.252414
H	1.499906	-1.381902	-1.513294
H	3.631997	0.090218	-1.867912
H	5.059290	-0.180801	-0.823892
H	5.385039	-1.187805	-3.103461
H	5.333603	-4.279292	-0.044397
H	1.831249	-3.628855	-2.536010
H	3.919498	-4.963936	-2.034559
H	2.918183	-4.774530	-0.570365
H	3.942720	-3.134842	-3.829898
H	2.961146	-1.659815	-3.627891
H	6.474587	-2.308100	-1.121829
H	6.022325	-3.514480	-2.354703
C	-1.067209	2.844850	0.892272
C	-0.017949	2.899743	-0.036061
C	-0.250756	2.102263	-1.302141
C	0.754359	1.149946	-1.659350
C	1.234264	3.692281	0.171760
C	-1.434804	2.395381	-2.171965
C	2.108486	3.950421	-0.923289
C	3.256445	4.757147	-0.768198
C	1.541180	4.309763	1.420739
C	-2.004510	1.412756	-3.027801
C	-3.060090	1.742719	-3.899808
C	-1.958331	3.716167	-2.211362
C	2.687089	5.114210	1.578591
C	3.559024	5.336079	0.484715
C	-3.017612	4.048177	-3.085653
C	-3.571292	3.063939	-3.934424
H	-0.989912	3.336558	1.868577
H	-2.068848	2.530086	0.593336
H	1.780823	1.258597	-1.301674
H	0.623858	0.564901	-2.574518
H	1.871729	3.545885	-1.912379
H	-1.641895	0.378658	-2.983442
H	0.867383	4.191401	2.278081
H	2.891941	5.585025	2.547327
H	4.446001	5.968690	0.603714
H	3.905582	4.945963	-1.630771
H	-1.525587	4.493022	-1.570131
H	-3.403486	5.073945	-3.107498
H	-4.392419	3.319769	-4.613983
H	-3.491822	0.970790	-4.547538
H	-1.785711	0.436239	-0.382059
H	-0.289326	-0.999138	-0.414161

Complex Cation Q

E = -2129.61673159 A.U.
 E + ZPE = -2128.682451 A.U.
 E + H = -2128.632742 A.U.
 E + G = -2128.765604 A.U.

Ir	-0.415815	0.006268	-0.049682
C	-0.338508	1.321426	-1.554147
N	-0.443045	1.049681	-2.916218
C	-0.346749	2.229252	-3.680312
C	-0.188921	3.268391	-2.794593
N	-0.192605	2.714094	-1.499786
N	1.056760	-1.414944	-1.016397
C	2.258987	-1.937214	-0.813152
O	2.549654	-3.061605	-1.603074
C	1.306392	-3.424679	-2.340113
C	0.406913	-2.174220	-2.171080
C	0.341620	-1.330194	-3.466480

C	-0.769540	-0.260242	-3.523338
H	-0.406398	2.229367	-4.764841
H	-0.095576	4.336316	-2.962201
H	0.887843	-4.327264	-1.862537
H	1.593544	-3.639687	-3.381470
H	-0.610396	-2.459301	-1.859364
H	0.125611	-2.039292	-4.290998
H	1.328709	-0.876610	-3.680499
H	-1.008814	-0.053409	-4.581299
H	-1.688098	-0.647150	-3.044065
C	-0.232557	3.553256	-0.302768
C	0.988314	4.029765	0.259139
C	0.901215	4.880551	1.389882
C	-0.349480	5.246960	1.927366
C	-1.541742	4.782362	1.336357
C	-1.513147	3.931120	0.203289
C	2.356193	3.702353	-0.356112
C	-2.825885	3.527688	-0.483179
C	-3.919104	3.066896	0.516004
C	-3.351812	4.711817	-1.348186
C	2.794710	4.834857	-1.332625
C	3.461423	3.481749	0.709579
C	3.440074	-1.603638	0.088110
C	4.708123	-1.433488	-0.833798
C	3.284513	-0.317447	0.943854
C	3.684800	-2.826869	1.047769
C	5.973997	-1.207363	0.036117
C	4.560911	-0.084559	1.804941
C	4.955396	-2.584181	1.906999
C	6.187737	-2.426895	0.974426
C	5.799350	0.080041	0.884446
C	4.774347	-1.295338	2.754391
H	1.818483	5.263033	1.849731
H	-0.394802	5.907088	2.801308
H	-2.506926	5.093706	1.750573
H	-2.625672	2.677984	-1.162229
H	2.258932	2.769150	-0.946854
H	-2.615088	5.017037	-2.114179
H	-4.285922	4.423487	-1.865514
H	-3.569498	5.593803	-0.716938
H	-3.567719	2.231248	1.147362
H	-4.244015	3.889310	1.180197
H	-4.812431	2.725347	-0.039657
H	3.778550	4.598412	-1.779480
H	2.071488	4.973263	-2.156025
H	2.885271	5.797603	-0.795309
H	3.153258	2.749240	1.477968
H	4.383809	3.111156	0.224615
H	3.723229	4.424464	1.224496
H	4.832201	-2.333614	-1.461576
H	4.553649	-0.568239	-1.510881
H	3.113732	0.553229	0.280535
H	2.415017	-0.412522	1.620267
H	2.804047	-2.961301	1.710215
H	3.796264	-3.749118	0.448708
H	5.100639	-3.455636	2.574875
H	6.846632	-1.098744	-0.637338
H	4.416253	0.836232	2.404129
H	6.704846	0.260481	1.496672
H	5.672654	0.960256	0.220784
H	5.668699	-1.126574	3.385612
H	3.907166	-1.404594	3.437827
H	6.334789	-3.348532	0.376113
H	7.103811	-2.281374	1.580126
C	-0.174898	-1.313014	1.819194
C	-1.485719	-1.749982	1.509663
C	-1.678998	-3.015834	0.690561
C	-0.822042	-4.054660	0.942525
C	-2.642926	-1.249861	2.333916
C	-3.711372	-2.135542	2.652819

C	-4.738505	-1.747367	3.539776
C	-4.724470	-0.462753	4.127612
C	-3.667324	0.428777	3.823119
C	-2.641766	0.038607	2.939719
C	-2.805405	-3.138295	-0.301266
C	-3.639573	-2.029429	-0.629314
C	-4.683910	-2.148789	-1.571108
C	-4.929480	-3.380471	-2.218419
C	-4.121431	-4.497569	-1.898604
C	-3.083491	-4.376870	-0.952463
H	0.677201	-1.923381	1.508344
H	-0.019233	-0.687539	2.704261
H	-3.733215	-3.142287	2.224050
H	-5.546742	-2.450327	3.771913
H	-5.524370	-0.159091	4.812799
H	-3.646057	1.428959	4.271731
H	-1.840339	0.746475	2.699305
H	-0.892128	-5.017451	0.426393
H	-0.054937	-3.986415	1.718922
H	-3.483481	-1.066622	-0.135897
H	-5.315033	-1.278861	-1.788161
H	-5.744950	-3.475571	-2.944717
H	-4.310491	-5.467089	-2.374375
H	-2.502247	-5.273201	-0.710685
H	-1.644331	0.853256	0.504996
H	-1.515295	-0.729558	-0.920788
H	1.031468	0.839606	0.758184
H	0.351574	1.264602	1.028705

Complex Cation R

E = -2128.45044271 A.U.
 E + ZPE = -2127.532818 A.U.
 E + H = -2127.484180 A.U.
 E + G = -2127.612923 A.U.

Ir	-0.455282	0.502911	0.129794
C	-1.140678	-0.850750	1.457556
N	-0.886734	-0.860424	2.829656
C	-1.377168	-2.035645	3.432868
C	-1.972655	-2.772092	2.439419
N	-1.849102	-2.041808	1.240565
N	1.646811	0.552651	1.143142
C	2.883842	0.139741	0.880879
O	3.864026	0.637324	1.760347
C	3.207960	1.646369	2.635806
C	1.706802	1.326430	2.457336
C	1.150221	0.489381	3.632014
C	-0.376673	0.271784	3.634262
H	-1.273050	-2.233719	4.495764
H	-2.480298	-3.730281	2.473266
H	3.485111	2.645735	2.259981
H	3.586998	1.493449	3.658452
H	1.133038	2.258406	2.349590
H	1.391256	1.042874	4.562381
H	1.677646	-0.482631	3.688417
H	-0.704548	0.079061	4.670980
H	-0.890892	1.184993	3.290098
C	-2.567496	-2.477263	0.036932
C	-1.959420	-3.421879	-0.838780
C	-2.723576	-3.891178	-1.937431
C	-4.042478	-3.447448	-2.147968
C	-4.632754	-2.535974	-1.250608
C	-3.918409	-2.039480	-0.132551
C	-0.556940	-3.991680	-0.593994
C	-4.634159	-1.127785	0.876716
H	-2.282072	-4.613795	-2.631242
H	-4.615370	-3.819877	-3.005011
H	-5.664123	-2.209991	-1.416312

C	-5.707887	-0.222306	0.217413
C	-5.316889	-1.974734	1.994357
C	-0.645069	-5.344308	0.173844
C	0.238162	-4.190047	-1.909925
H	-3.877697	-0.471688	1.351905
H	0.003728	-3.277189	0.040915
H	-4.591015	-2.567332	2.576966
H	-5.857006	-1.313170	2.697964
H	-6.052225	-2.671892	1.550315
H	-5.320079	0.287813	-0.680611
H	-6.601273	-0.804846	-0.076179
H	-6.048673	0.542715	0.940954
H	0.367314	-5.756226	0.345153
H	-1.136326	-5.231390	1.157250
H	-1.221422	-6.086471	-0.409850
H	0.271594	-3.260936	-2.507951
H	1.273790	-4.499054	-2.682370
H	-0.204017	-4.985731	-2.537094
C	3.541812	-0.803102	-0.123716
C	4.197092	-1.972976	0.713784
C	2.602287	-1.434267	-1.184939
C	4.700951	-0.029201	-0.857620
C	4.999003	-2.918853	-0.221582
C	3.410680	-2.386097	-2.116126
C	5.493726	-0.988893	-1.783028
C	6.126949	-2.123165	-0.932944
C	4.046378	-3.530962	-1.280752
C	4.533327	-1.595475	-2.840199
H	4.864157	-1.546585	1.484596
H	3.398471	-2.541491	1.233933
H	1.795253	-2.000210	-0.683381
H	2.117322	-0.646253	-1.791620
H	4.274193	0.791639	-1.467280
H	5.373579	0.425884	-0.108623
H	6.292656	-0.410793	-2.287807
H	5.443240	-3.724450	0.395683
H	2.716612	-2.811635	-2.866196
H	4.604810	-4.220182	-1.944829
H	3.258356	-4.129381	-0.778567
H	5.090667	-2.268769	-3.520884
H	4.094157	-0.790208	-3.464712
H	6.825592	-1.696711	-0.185385
H	6.714850	-2.801189	-1.582427
C	-1.350478	2.578805	1.180240
C	-1.323437	2.654347	-0.233000
C	0.036874	2.496766	-0.865241
C	0.102055	1.478883	-1.868749
C	-2.530355	2.915394	-1.072361
C	1.184898	3.366236	-0.468194
C	-3.849299	2.667180	-0.608077
C	-4.968553	3.041530	-1.377450
C	-2.366043	3.553012	-2.334692
C	0.942396	4.604786	0.194333
C	2.005016	5.480256	0.507981
C	2.524160	3.056662	-0.830248
C	-3.486165	3.928137	-3.107046
C	-4.792567	3.675030	-2.631338
C	3.586113	3.928456	-0.519612
C	3.333805	5.145182	0.159299
H	-0.469090	2.851126	1.760547
H	-2.305563	2.602412	1.714666
H	-0.778903	1.219179	-2.460693
H	1.061869	1.235132	-2.333462
H	-4.002373	2.165145	0.353871
H	-0.084068	4.902534	0.434032
H	-1.358958	3.780399	-2.701880
H	-3.339338	4.425819	-4.072476
H	-5.664164	3.969487	-3.227109
H	-5.979412	2.840853	-1.003406
H	2.737925	2.130344	-1.370814
H	4.608830	3.664972	-0.814277

H	4.157059	5.830425	0.391783
H	1.792714	6.434183	1.004600
H	-1.818294	0.217967	-0.631051
H	0.082974	-0.826943	-0.552240

Complex Cation S

E = -2129.61722481 A.U.
E + ZPE = -2128.684046 A.U.
E + H = -2128.634052 A.U.

E + G = -2128.768627 A.U.

Ir	-0.428141	0.371062	0.465266
C	-1.737125	-0.745121	1.505330
N	-1.702311	-1.043079	2.863806
C	-2.812910	-1.822179	3.244106
C	-3.568446	-2.019166	2.112883
N	-2.914625	-1.355915	1.056621
N	1.397325	-0.691996	1.304986
C	2.420796	-1.432214	0.900175
O	3.466559	-1.543496	1.827913
C	3.134573	-0.677603	2.995693
C	1.647605	-0.302171	2.758692
C	0.709081	-1.045900	3.740411
C	-0.735128	-0.512143	3.849408
H	-2.971180	-2.155387	4.265680
H	-4.506143	-2.545037	1.967310
H	3.810059	0.191662	2.968756
H	3.307333	-1.278224	3.903161
H	1.499059	0.785847	2.847064
H	1.155873	-0.924934	4.748102
H	0.705489	-2.130850	3.519432
H	-1.137126	-0.777474	4.842867
H	-0.734287	0.591110	3.775361
C	-3.524678	-1.232444	-0.266896
C	-3.362132	-2.291212	-1.208672
C	-4.018562	-2.163351	-2.458784
C	-4.808061	-1.032945	-2.751608
C	-4.970562	-0.012226	-1.793682
C	-4.340535	-0.090175	-0.526548
C	-2.567044	-3.564554	-0.886091
C	-4.617369	0.990611	0.528112
C	-4.512447	2.429411	-0.042925
C	-6.020311	0.760693	1.164369
C	-3.527002	-4.692846	-0.402833
C	-1.733587	-4.075032	-2.090989
C	2.739715	-2.239867	-0.353122
C	3.102616	-3.702826	0.113215
C	1.594752	-2.335964	-1.397976
C	4.006907	-1.614014	-1.044350
C	3.548392	-4.560623	-1.101004
C	2.038050	-3.209218	-2.609790
C	4.439068	-2.486535	-2.254550
C	4.797060	-3.915597	-1.762349
C	2.393212	-4.642655	-2.133337
C	3.279266	-2.564153	-3.284395
H	-3.914883	-2.956817	-3.206472
H	-5.307397	-0.953358	-3.724075
H	-5.601778	0.852149	-2.026750
H	-3.863846	0.903207	1.333030
H	-1.866348	-3.340085	-0.056708
H	-6.096380	-0.236249	1.636968
H	-6.219917	1.524149	1.939404
H	-6.816517	0.834493	0.399886
H	-3.528360	2.603590	-0.514973
H	-5.299024	2.634088	-0.792865
H	-4.639040	3.165121	0.773552
H	-2.957008	-5.613370	-0.176657

H	-4.081535	-4.403405	0.507912	C	-2.927563	-0.434119	-0.780093
H	-4.267689	-4.932722	-1.188548	O	-4.061075	-0.071342	-1.522166
H	-1.111561	-3.274071	-2.530377	C	-3.647082	0.950254	-2.524468
H	-1.066814	-4.896393	-1.768089	C	-2.097498	0.940483	-2.438627
H	-2.380234	-4.478715	-2.891683	C	-1.464855	0.322595	-3.706349
H	3.908481	-3.661344	0.866736	C	0.054998	0.530273	-3.864250
H	2.215437	-4.161192	0.597220	H	1.578790	-1.541799	-4.962512
H	0.693552	-2.773544	-0.924912	H	3.172356	-2.865023	-3.093722
H	1.334968	-1.328052	-1.771960	H	-4.093628	1.911863	-2.226361
H	3.771705	-0.586418	-1.392601	H	-4.042581	0.626024	-3.500873
H	4.829309	-1.539237	-0.309071	H	-1.705081	1.958477	-2.287747
H	5.327139	-2.020750	-2.724991	H	-1.939769	0.829640	-4.570745
H	3.801443	-5.576007	-0.738134	H	-1.720985	-0.751969	-3.783429
H	1.201610	-3.252455	-3.335238	H	0.316792	0.469829	-4.935315
H	2.697209	-5.263792	-2.998801	H	0.333621	1.538176	-3.507714
H	1.506291	-5.129052	-1.677661	C	2.996217	-1.840031	-0.543884
H	3.588997	-3.168357	-4.159637	C	2.635984	-2.955449	0.267490
H	3.030212	-1.550642	-3.661196	C	3.492219	-3.284332	1.348461
H	5.634246	-3.871812	-1.036944	C	4.665161	-2.544243	1.596397
H	5.135690	-4.535382	-2.615629	C	5.019833	-1.472072	0.753790
C	0.879354	1.371279	-1.102443	C	4.202094	-1.100774	-0.342285
C	0.827716	2.366883	-0.095138	C	1.417352	-3.836114	-0.040159
C	-0.088119	3.573430	-0.312348	C	4.672409	-0.009761	-1.316083
C	-1.072975	3.940580	0.554708	C	5.374412	1.180336	-0.613384
C	1.994277	2.606157	0.840372	C	5.637816	-0.621899	-2.376543
C	3.303557	2.152880	0.513366	C	1.841485	-5.056437	-0.911383
C	4.406815	2.443734	1.344877	C	0.699983	-4.339328	1.238849
C	4.227542	3.191625	2.531667	C	-3.313439	-1.438646	0.300584
C	2.933058	3.655279	2.868216	C	-4.055204	-2.628772	-0.422690
C	1.835677	3.374220	2.027218	C	-2.136993	-2.026223	1.125377
C	0.214489	4.395633	-1.531987	C	-4.332817	-0.751743	1.284817
C	-0.829688	5.094589	-2.202987	C	-4.583893	-3.648013	0.620508
C	-0.561126	5.892142	-3.334953	C	-2.670269	-3.058808	2.161919
C	0.759478	6.004156	-3.829974	C	-4.853533	-1.785689	2.320331
C	1.805144	5.304892	-3.184108	C	-5.580757	-2.941533	1.580467
C	1.534656	4.505377	-2.053283	C	-3.394049	-4.222709	1.433119
H	0.268653	1.501278	-2.001184	C	-3.659748	-2.357659	3.132253
H	1.757625	0.726962	-1.209536	H	3.243416	-4.130589	1.997185
H	3.478341	1.606374	-0.419836	H	5.312462	-2.813659	2.438926
H	5.408215	2.105800	1.053836	H	5.947815	-0.922170	0.942973
H	5.085778	3.432663	3.169435	H	3.789807	0.393199	-1.848505
H	2.783633	4.256846	3.772246	H	0.692743	-3.238448	-0.629454
H	0.848328	3.775375	2.276687	H	5.159411	-1.429336	-2.958718
H	-1.633705	4.870896	0.413538	H	5.969941	0.159019	-3.086137
H	-1.347315	3.315994	1.409288	H	6.536080	-1.042057	-1.885957
H	-1.862213	4.990310	-1.848604	H	4.763242	1.573271	0.215592
H	-1.381984	6.416635	-3.838173	H	6.362072	0.891469	-0.207882
H	0.968918	6.623069	-4.710066	H	5.548232	1.994427	-1.341217
H	2.832670	5.388008	-3.557261	H	0.965562	-5.694511	-1.132976
H	2.363785	3.989770	-1.555508	H	2.286237	-4.743399	-1.872892
H	-1.656413	1.269985	0.010387	H	2.587952	-5.673010	-0.376332
H	-0.403416	1.292572	1.766903	H	0.465093	-3.510970	1.932104
H	-1.095586	-0.426825	-1.022621	H	-0.244715	-4.846501	0.968704
H	-0.420948	-0.917944	-0.858873	H	1.316416	-5.075583	1.786922
-----				H	-4.892106	-2.230439	-1.022597
Complex Cation T				H	-3.350025	-3.128594	-1.118294
E	= -2130.83374733 A.U.			H	-1.410341	-2.514114	0.446944
E + ZPE	= -2129.876933 A.U.			H	-1.611333	-1.219436	1.668273
E + H	= -2129.827485 A.U.			H	-3.833377	0.085993	1.815697
E + G	= -2129.957976 A.U.			H	-5.174234	-0.328735	0.706179
-----				H	-5.561474	-1.274718	3.001885
Ir	0.302470	0.585400	-0.377898	H	-5.101659	-4.465166	0.081035
C	1.195510	-0.500763	-1.811808	H	-1.809799	-3.455303	2.735218
N	0.914820	-0.456583	-3.176725	H	-3.755615	-4.964497	2.172292
C	1.660109	-1.416923	-3.886663	H	-2.690867	-4.751511	0.756751
C	2.443768	-2.071089	-2.967997	H	-4.025741	-3.081695	3.886730
N	2.174420	-1.501985	-1.707935	H	-3.145367	-1.544087	3.684434
N	-1.795758	0.134176	-1.177063	H	-6.445398	-2.546309	1.010136
				H	-5.979698	-3.668912	2.314614
				C	-0.815763	1.384252	1.469064
				C	-0.434161	2.607462	0.883338

C	-1.405206	3.373929	0.013091
C	-2.798347	3.350942	0.289537
C	-3.706184	4.124539	-0.470514
C	-3.237475	4.938040	-1.527069
C	-1.849118	4.977758	-1.809235
C	-0.947676	4.210277	-1.043556
H	-1.828815	1.001226	1.318343

H	-3.175902	2.757047	1.130231
H	-4.773928	4.107756	-0.221731
H	-3.937630	5.548787	-2.108787
H	-1.471409	5.617620	-2.615419
H	0.124603	4.256782	-1.269758
H	1.740406	1.120909	0.051284
H	0.344462	1.792275	-1.412007
H	0.177601	-0.961285	0.638628
H	0.920606	-0.607200	0.847267
H	-0.280211	1.012850	2.346083
C	0.743040	3.458608	1.440100
C	0.165725	4.765100	2.084074
H	-0.535660	4.532917	2.905951
H	0.997084	5.357903	2.504578
C	1.662924	2.769163	2.452557
C	3.469905	1.656641	4.365101
C	3.032185	2.583818	2.142742
C	1.216471	2.403025	3.751683
C	2.107570	1.847863	4.696421
C	3.931371	2.033729	3.084027
H	3.398392	2.897109	1.156606
H	0.172638	2.576605	4.043779
H	1.743356	1.578590	5.695207
H	4.989411	1.909495	2.822591
H	4.163737	1.235478	5.102079
H	1.366894	3.768995	0.578986
H	-0.367288	5.387210	1.346065

Complex Cation U

E = -2130.82956639 A.U.

E + ZPE = -2129.872715 A.U.

E + H = -2129.822288 A.U.

E + G = -2129.957205 A.U.

Ir	0.193442	0.355024	0.492756
C	-0.996739	1.595920	1.507058
N	-1.189176	1.647444	2.884857
C	-2.060163	2.693325	3.245762
C	-2.429267	3.321810	2.081342
N	-1.783172	2.653973	1.023037
N	-0.692013	-1.508743	1.472222
C	-1.328601	-2.623970	1.135839
O	-1.345790	-3.615744	2.128649
C	-0.535910	-3.128746	3.278475
C	-0.253647	-1.640533	2.930199
C	-0.996328	-0.684734	3.893272
C	-0.528903	0.786740	3.885210
H	-2.329536	2.901149	4.277197
H	-3.067953	4.181971	1.910470
H	0.372572	-3.751442	3.333250
H	-1.144583	-3.264678	4.187008
H	0.826608	-1.420983	2.969999
H	-0.803185	-1.067507	4.915910
H	-2.089442	-0.744493	3.729287
H	-0.743370	1.236993	4.870226
H	0.563606	0.837523	3.724284
C	-1.889293	3.136200	-0.353966
C	-3.018826	2.751127	-1.137318
C	-3.122481	3.287663	-2.445441

C	-2.148694	4.176037	-2.945350
C	-1.058120	4.560974	-2.140483
C	-0.907219	4.059033	-0.823365
C	-4.131865	1.845665	-0.589805
C	0.229785	4.577127	0.066902
C	1.580459	4.690378	-0.684816
C	-0.166667	5.954184	0.678446
C	-5.293750	2.703938	-0.004366
C	-4.707629	0.877643	-1.657217
C	-2.067219	-3.106561	-0.105385
C	-3.496536	-3.594223	0.347234
C	-2.243813	-2.046352	-1.224145
C	-1.288236	-4.344031	-0.690605
C	-4.260724	-4.202774	-0.858901
C	-3.022634	-2.653766	-2.427329
C	-2.067998	-4.939652	-1.894966
C	-3.468445	-5.415646	-1.420623
C	-4.426288	-3.129382	-1.966372
C	-2.228184	-3.860374	-3.000009
H	-3.974833	3.013004	-3.075841
H	-2.247733	4.579241	-3.959837
H	-0.318430	5.266575	-2.533172
H	0.378107	3.866406	0.901129
H	-3.713052	1.236246	0.236169
H	-1.088050	5.883403	1.285734
H	0.644385	6.331565	1.328961
H	-0.341512	6.701799	-0.118135
H	1.856225	3.737735	-1.170630
H	1.556529	5.480374	-1.458954
H	2.383543	4.954793	0.027647
H	-6.097095	2.049884	0.383800
H	-4.956853	3.353225	0.822839
H	-5.729019	3.351495	-0.788507
H	-3.912847	0.324100	-2.189284
H	-5.380672	0.144811	-1.174422
H	-5.307865	1.417742	-2.412319
H	-3.394677	-4.343618	1.151931
H	-4.063164	-2.734080	0.759671
H	-2.792182	-1.171810	-0.823729
H	-1.257141	-1.700497	-1.580474
H	-0.276615	-4.026391	-1.018474
H	-1.159818	-5.107226	0.098928
H	-1.495480	-5.800504	-2.292232
H	-5.256529	-4.538322	-0.508868
H	-3.128915	-1.873753	-3.207784
H	-4.985019	-3.549484	-2.825737
H	-5.015660	-2.272469	-1.581196
H	-2.763200	-4.285988	-3.871453
H	-1.231779	-3.528841	-3.358640
H	-3.363500	-6.198905	-0.643212
H	-4.020737	-5.868757	-2.267324
C	1.312362	-1.021729	-1.046808
C	2.476625	-0.554149	-0.414563
C	3.222381	0.643113	-0.939588
C	3.222244	0.946278	-2.328325
C	3.978735	2.023872	-2.837453
C	4.753142	2.822521	-1.965317
C	4.760715	2.534035	-0.579761
C	4.007650	1.455189	-0.076362
H	0.958176	-2.037619	-0.851711
H	2.659474	0.314480	-3.025558
H	3.977752	2.227501	-3.914615
H	5.349024	3.653683	-2.360012
H	5.359658	3.145909	0.104775
H	4.018788	1.252632	1.000747
H	0.966514	1.655127	0.005523
H	1.213180	0.405020	1.719406
H	-1.118616	0.185022	-0.796266
H	-0.679477	0.880590	-1.009018
H	0.989725	-0.574566	-1.993083
C	3.249850	-1.417789	0.616529

C	2.584023	-2.774429	0.959428
H	2.595976	-3.453519	0.087309
H	3.156204	-3.269796	1.764384
C	4.685050	-1.699674	0.122185
C	7.324012	-2.378692	-0.701548
C	5.788102	-1.487320	0.984668
C	4.920558	-2.261637	-1.158432
C	6.228943	-2.594743	-1.571041
C	7.099717	-1.824623	0.579557
H	5.622923	-1.056017	1.981570
H	4.079548	-2.433413	-1.843899
H	6.396081	-3.022264	-2.567000
H	7.942884	-1.655135	1.259810
H	8.340487	-2.638488	-1.019618
H	3.341969	-0.829533	1.550459
H	1.539374	-2.652951	1.285686

Complex Cation V

E = -2130.83868739 A.U.
E + ZPE = -2129.880756 A.U.
E + H = -2129.830759 A.U.
E + G = -2129.962833 A.U.

Ir	-0.124806	-0.521436	0.272952
C	1.192358	-1.464310	1.447980
N	1.281947	-1.401382	2.835336
C	2.329862	-2.210857	3.316327
C	2.910446	-2.805437	2.221275
N	2.210226	-2.356221	1.084886
N	0.160702	1.491980	1.269036
C	0.571908	2.720686	0.982090
O	0.202177	3.696796	1.918107
C	-0.655083	3.041883	2.947341
C	-0.490834	1.528072	2.649169
C	0.372659	0.826564	3.725669
C	0.330620	-0.716277	3.737777
H	2.562475	-2.299021	4.373603
H	3.731861	-3.510581	2.148169
H	-1.686046	3.401782	2.803240
H	-0.270078	3.349221	3.932981
H	-1.473139	1.035377	2.573606
H	-0.028777	1.152032	4.706689
H	1.419170	1.183928	3.670877
H	0.568599	-1.071406	4.755849
H	-0.689743	-1.065136	3.493183
C	2.443190	-2.929064	-0.240502
C	3.466358	-2.382482	-1.069865
C	3.687697	-2.997382	-2.328168
C	2.927968	-4.113157	-2.734710
C	1.941272	-4.649728	-1.883593
C	1.679832	-4.076101	-0.614173
C	4.353115	-1.214699	-0.615455
C	0.671916	-4.745826	0.330844
C	-0.661350	-5.116670	-0.369977
C	1.313538	-6.011294	0.973431
C	5.671310	-1.751865	0.018006
C	4.693708	-0.232098	-1.766288
C	1.404340	3.347509	-0.130441
C	2.613234	4.090452	0.559293
C	1.976699	2.353316	-1.175634
C	0.526370	4.420872	-0.874254
C	3.457073	4.842774	-0.503304
C	2.829709	3.111240	-2.234613
C	1.385773	5.170287	-1.929249
C	2.565503	5.892832	-1.222220
C	4.015297	3.832060	-1.538889
C	1.942033	4.156197	-2.964882
H	4.463401	-2.602790	-2.992829

H	3.115050	-4.573506	-3.711713
H	1.373983	-5.530909	-2.202984
H	0.426890	-4.041638	1.147627
H	3.810541	-0.649345	0.168882
H	2.234451	-5.762837	1.532791
H	0.603635	-6.488130	1.674873
H	1.578754	-6.754647	0.198238
H	-1.122387	-4.234283	-0.848804
H	-0.519612	-5.892432	-1.145000
H	-1.374334	-5.521870	0.372081
H	6.313216	-0.911752	0.343211
H	5.476386	-2.390616	0.898120
H	6.238945	-2.351784	-0.717793
H	3.788021	0.100485	-2.305821
H	5.205405	0.660934	-1.361629
H	5.377994	-0.691156	-2.503736
H	2.228550	4.800098	1.312845
H	3.244056	3.347414	1.089545
H	2.602695	1.594832	-0.665796
H	1.152734	1.829922	-1.695060
H	-0.329040	3.920269	-1.375036
H	0.111738	5.133452	-0.137814
H	0.744859	5.914903	-2.440523
H	4.293616	5.354387	0.011718
H	3.216742	2.375520	-2.966996
H	4.634448	4.357822	-2.291982
H	4.672085	3.093385	-1.034442
H	2.537719	4.686741	-3.733368
H	1.107381	3.650046	-3.492495
H	2.180003	6.631757	-0.491336
H	3.165289	6.453059	-1.966328
C	-1.310324	0.598234	-1.370711
C	-2.368217	0.014018	-0.645235
C	-3.130575	0.811177	0.386802
C	-3.256892	2.221656	0.274940
C	-4.020367	2.962763	1.204940
C	-4.673375	2.306529	2.273267
C	-4.562392	0.899400	2.394040
C	-3.806734	0.164449	1.458209
H	-1.044342	1.647705	-1.211445
H	-2.793909	2.745344	-0.569482
H	-4.125064	4.047059	1.079601
H	-5.279309	2.877152	2.986680
H	-5.080877	0.375676	3.205755
H	-3.741820	-0.924999	1.560859
H	-0.514698	-1.964110	-0.271857
H	-1.192088	-0.843896	1.406376
H	1.260549	-0.042627	-0.861790
H	1.009786	-0.808367	-1.122783
H	-1.004075	0.169046	-2.328552
C	-3.072858	-1.278037	-1.146376
C	-2.409649	-1.945101	-2.379651
H	-2.490303	-1.301985	-3.275300
H	-1.343846	-2.178789	-2.202456
C	-4.552359	-0.995515	-1.479204
C	-7.276737	-0.592228	-2.205123
C	-5.567589	-1.848819	-0.981262
C	-4.920594	0.061726	-2.350277
C	-6.270901	0.266361	-2.708146
C	-6.920638	-1.652777	-1.340766
H	-5.298904	-2.677223	-0.311391
H	-4.149863	0.734907	-2.749571
H	-6.539798	1.090630	-3.379783
H	-7.693564	-2.324983	-0.949238
H	-8.325424	-0.436755	-2.484542
H	-3.057555	-2.012050	-0.317085
H	-2.937799	-2.887736	-2.608202

Complex Cation W

E = -2130.82649214 A.U.

E + ZPE = -2129.870677 A.U.

E + H = -2129.820750 A.U.

E + G = -2129.953622 A.U.

Ir	0.113588	-0.471987	0.528284
C	1.821757	-0.599362	1.547999
N	2.024161	-0.386900	2.910246
C	3.375329	-0.578097	3.261919
C	4.041960	-0.928315	2.112184
N	3.094155	-0.946847	1.071093
N	-0.456497	1.528170	1.457417
C	-0.683041	2.790251	1.113927
O	-1.356120	3.550708	2.084471
C	-1.756587	2.625415	3.181548
C	-0.913435	1.353821	2.904378
C	0.277483	1.221249	3.883843
C	0.970234	-0.157670	3.922284
H	3.736701	-0.462459	4.279742
H	5.083672	-1.181385	1.944670
H	-2.844385	2.459169	3.096647
H	-1.520581	3.124211	4.134646
H	-1.533763	0.443325	2.955831
H	-0.130466	1.390115	4.901023
H	1.017894	2.022662	3.696269
H	1.457488	-0.283309	4.905024
H	0.215706	-0.959549	3.820081
C	3.426493	-1.449185	-0.261701
C	4.007209	-0.562140	-1.215575
C	4.368425	-1.100087	-2.476624
C	4.164222	-2.464203	-2.768550
C	3.609263	-3.323856	-1.799065
C	3.235990	-2.840521	-0.519885
C	4.299015	0.910558	-0.894741
C	2.735811	-3.821291	0.550109
C	1.683431	-4.825621	0.010940
C	3.944468	-4.586093	1.167485
C	5.777467	1.083040	-0.434531
C	4.015673	1.855087	-2.092337
C	-0.367698	3.642220	-0.106039
C	0.426503	4.909412	0.394849
C	0.474368	2.939068	-1.203826
C	-1.725592	4.129211	-0.736918
C	0.690340	5.877459	-0.789044
C	0.747920	3.916832	-2.383943
C	-1.443072	5.099217	-1.916575
C	-0.663150	6.338521	-1.396919
C	1.532063	5.156229	-1.874635
C	-0.602137	4.372943	-3.001517
H	4.817138	-0.447884	-3.233240
H	4.451678	-2.860717	-3.749283
H	3.475812	-4.386225	-2.030512
H	2.251640	-3.246054	1.361031
H	3.646827	1.219731	-0.053173
H	4.681214	-3.894976	1.617554
H	3.596613	-5.278287	1.957027
H	4.467113	-5.183279	0.396690
H	0.825135	-4.307341	-0.453215
H	2.116608	-5.513666	-0.738985
H	1.302512	-5.447604	0.842268
H	5.986651	2.143692	-0.200517
H	6.002579	0.484893	0.466714
H	6.472695	0.765511	-1.234237
H	3.005674	1.695719	-2.512533
H	4.095807	2.909859	-1.769338
H	4.748788	1.709332	-2.906957
H	-0.152815	5.420935	1.183951
H	1.389256	4.584898	0.841101
H	1.433963	2.591500	-0.773306
H	-0.070808	2.058504	-1.590407

H	-2.301642	3.253374	-1.101447
H	-2.333142	4.632103	0.037645
H	-2.411894	5.421016	-2.345990
H	1.245072	6.755990	-0.405456
H	1.345933	3.384733	-3.150114
H	1.740713	5.844831	-2.716854
H	2.511602	4.846708	-1.455143
H	-0.416176	5.053492	-3.855495
H	-1.159250	3.498670	-3.396894
H	-1.261513	6.875760	-0.633915
H	-0.481435	7.046811	-2.229061
C	-1.692729	-0.060297	-0.874853
C	-1.223694	-1.292246	-0.436167
C	-2.114005	-2.514772	-1.299487
C	-1.024886	-2.700053	-2.200208
C	-0.980408	-3.796699	-3.081943
C	-2.030109	-4.747186	-3.090775
C	-3.119338	-4.580894	-2.207291
C	-3.159423	-3.482758	-1.321544
H	-2.078849	0.864665	-0.432796
H	-0.186045	-1.995529	-2.181680
H	-0.124133	-3.915617	-3.756257
H	-1.997345	-5.602500	-3.775575
H	-3.945424	-5.301312	-2.210563
H	-4.037426	-3.357790	-0.683050
H	0.374288	-1.985597	0.112660
H	-0.598269	-1.129993	1.786198
H	0.973071	0.489560	-0.794307
H	1.091290	-0.325373	-0.998627
H	-1.305432	0.022515	-1.896553
C	-3.212377	-1.273922	0.753380
C	-3.033105	-2.454208	1.749395
H	-3.513285	-3.383543	1.400733
H	-1.960223	-2.665236	1.893569
C	-4.684093	-1.095777	0.277714
C	-7.408315	-0.643090	-0.476599
C	-5.756491	-1.585993	1.071048
C	-5.008957	-0.375260	-0.902868
C	-6.352390	-0.154111	-1.278734
C	-7.102140	-1.361249	0.701025
H	-5.552755	-2.151920	1.986449
H	-4.213174	0.007415	-1.551890
H	-6.573561	0.396223	-2.201157
H	-7.909707	-1.750335	1.332769
H	-8.451451	-0.472441	-0.767017
H	-2.968449	-0.344844	1.309886
H	-3.467267	-2.200240	2.733629

