

## Supporting Information

Experimental and Computational Study of a Direct O<sub>2</sub>-Coupled Wacker Oxidation: Water

Dependence in the Absence of Cu Salts

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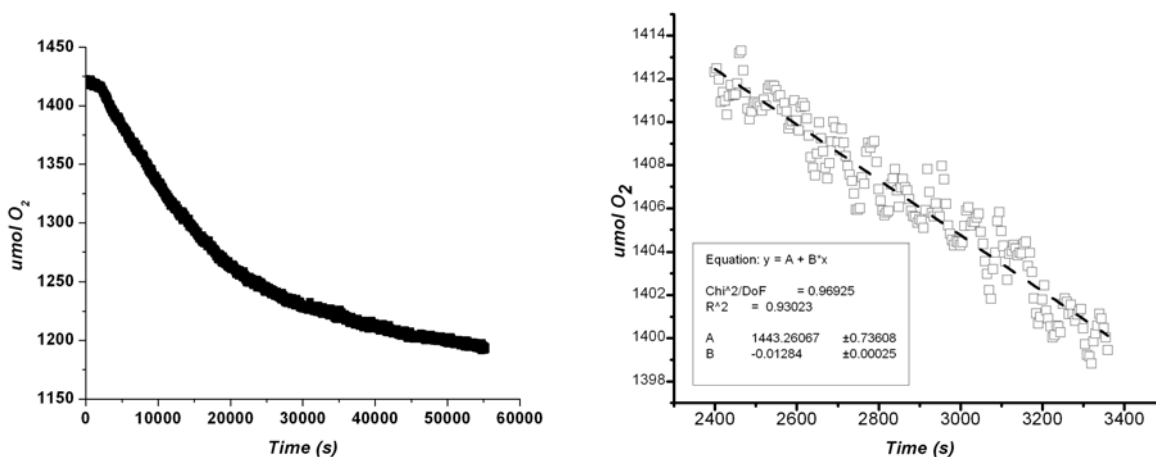
## General

All reagents, unless otherwise specified were bought from commercial sources and used without further purification. **Caution should be taken when heating flammable solvents in the presence of O<sub>2</sub>.** Pd((-)-sparteine)Cl<sub>2</sub> was prepared as described by literature procedure.<sup>i</sup>

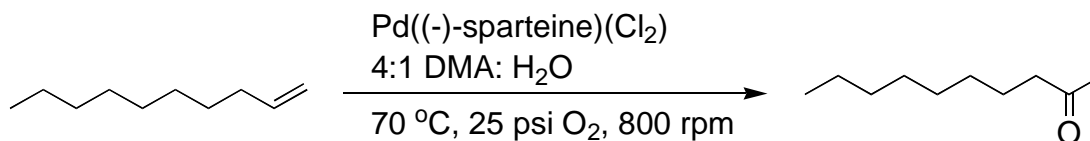
### Sample experiment to determine initial rate:

Water (0.27 mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69 μL of a 0.029M solution in DMA, 0.002 mmol), and DMA (1.35 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The reaction vessel was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi O<sub>2</sub> and heated to 70 °C. The mixture was stirred at 800 rpm for 20 minutes (allowing the pressure to stabilize) before decene (114 μL, 0.6 mmol, 0.3 M) was injected via syringe. Pressure data was collected every five seconds and converted to μmol of O<sub>2</sub>. The conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. After a short incubation period (approximately 15 min) the pressure decreased. The initial rate of the reaction was determined for the first two percent conversion of decene (loss of 12 μmol of O<sub>2</sub>, Figure 1).

**Figure 1.** Consumption of O<sub>2</sub> during Wacker oxidation of decene, the full reaction profile (left) and the linear fit for the initial two percent conversion of decene (right) are shown below.



### Dependence on decene

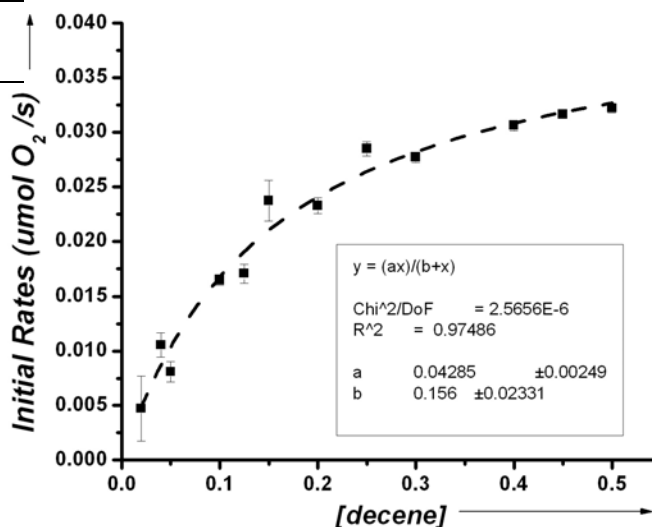


Water (0.4 mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69 μL of a 0.029M solution in DMA), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the pressure stabilized. Decene was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to μmol of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

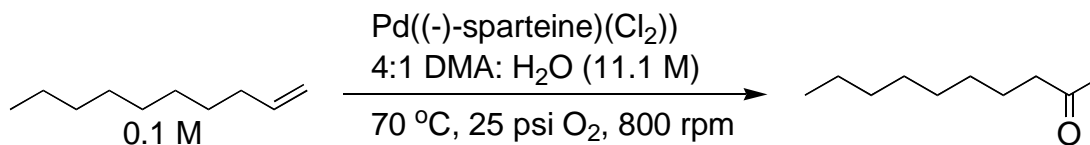
**Table 1.** Initial rates for oxidation of decene

[Decene]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
0.02	0.00305	4.20E-04
0.04	0.00786	2.30E-04
0.05	0.01283	2.10E-04
0.10 <sup>a</sup>	0.016	9.43E-05
0.125	0.02088	1.80E-04
0.15	0.02176	3.90E-04
0.20 <sup>a</sup>	0.01984	1.17E-04
0.25	0.03026	1.33E-04
0.30	0.02849	8.06E-05
0.40 <sup>a</sup>	0.0308	8.94E-05
0.45 <sup>a</sup>	0.03081	6.02E-05
0.50 <sup>a</sup>	0.02831	9.00E-05

<sup>a</sup> average of 2 values



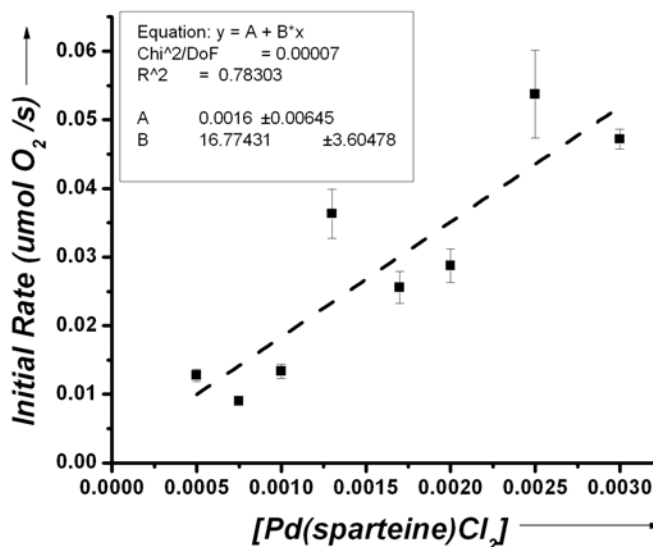
**Pd((-)-sparteine)(Cl<sub>2</sub>) dependence at low [decene] (0.1 M)**



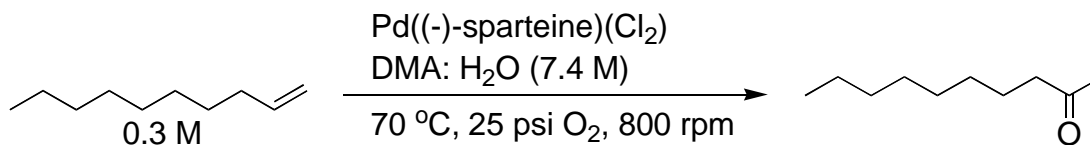
Water (0.4 mL, 11.1 M), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (x  $\mu\text{L}$  of a 0.029M solution in DMA), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi with O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene (38  $\mu\text{L}$ , 0.1 M) was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

[Pd]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
0.00050 <sup>a</sup>	0.01278	8.79E-04
0.00075 <sup>a</sup>	0.00898	4.20E-04
0.00100 <sup>a</sup>	0.01336	0.00102
0.00130	0.03631	0.0036
0.00170	0.02558	0.00232
0.00200 <sup>a</sup>	0.02873	0.00242
0.00250	0.05374	0.00641
0.00300	0.04717	0.00146

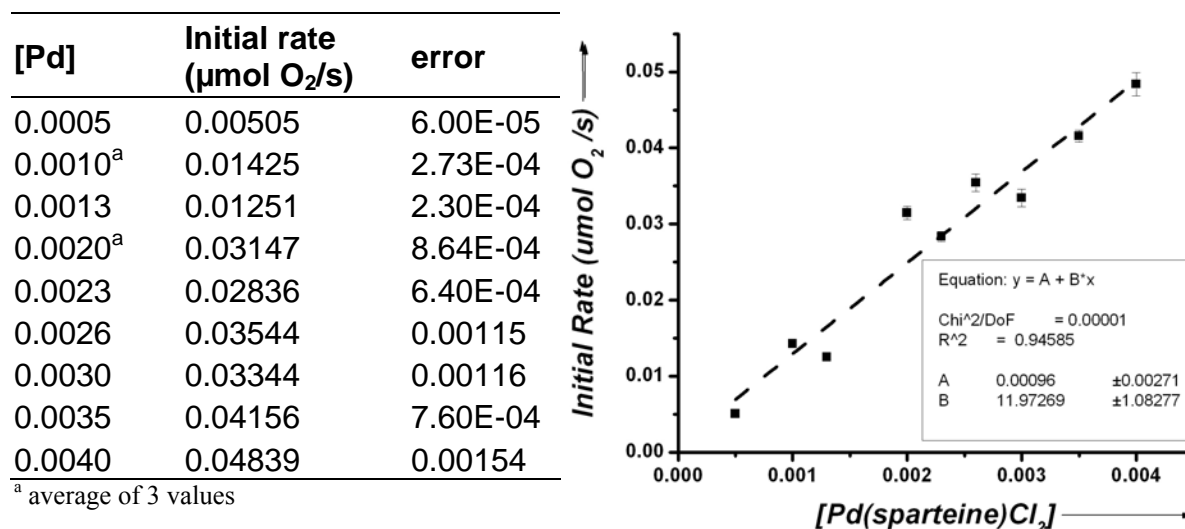
<sup>a</sup> average of at least 2 values



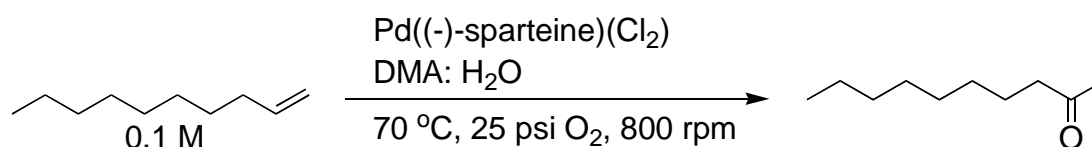
#### Pd((-)-sparteine)(Cl<sub>2</sub>) dependence at high [decene] (0.3 M)



Water (0.27 mL, 7.4 M), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (x  $\mu\text{L}$  of a 0.029M solution in DMA), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi with O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene (114  $\mu\text{L}$ , 0.3 M) was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.



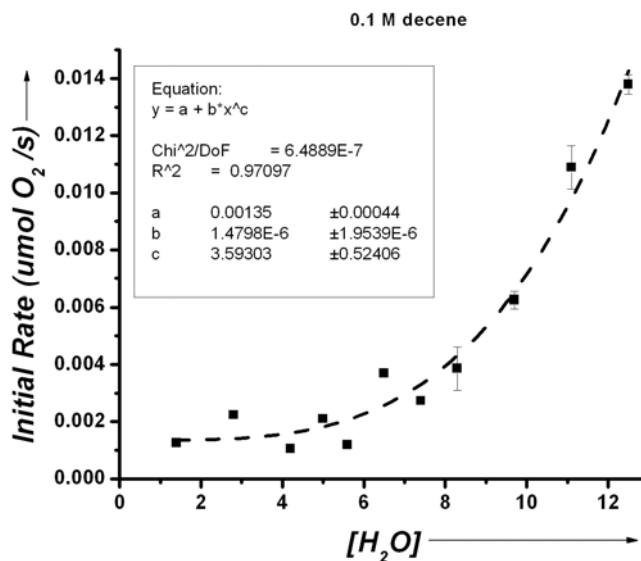
#### Water dependence at low [decene] (0.1 M)



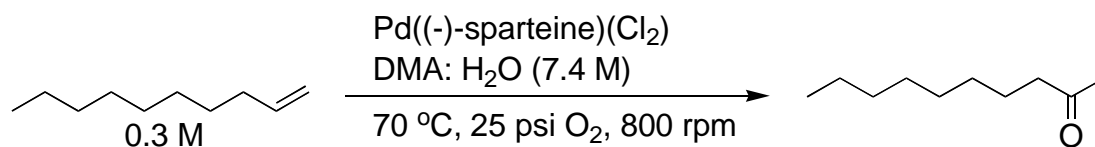
Water (x mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69  $\mu\text{L}$  of a 0.029M solution in DMA, 0.002 mmol), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi with O<sub>2</sub>, heated to 70  $^\circ\text{C}$ , and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene (38  $\mu\text{L}$ , 0.1 M) was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

[water]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
1.4	0.00126	3.00E-05
2.8 <sup>a</sup>	0.00224	6.08E-05
4.2	0.00105	3.00E-05
5.0	0.0021	9.00E-05
5.6	0.00118	5.00E-05
6.5	0.0037	1.00E-04
7.4	0.00273	6.00E-05
8.3	0.00386	7.60E-04
9.7	0.00625	3.00E-04
11.1 <sup>a</sup>	0.01089	7.61E-04
12.5	0.0138	3.40E-04

<sup>a</sup> average of 2 values



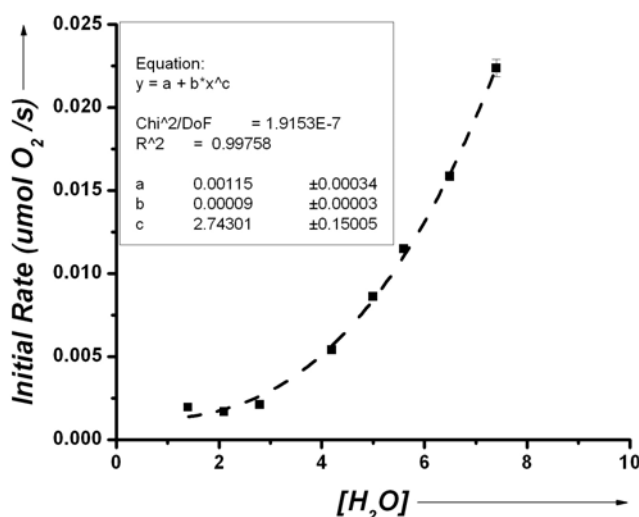
#### Water dependence at high [decene] (0.3 M)



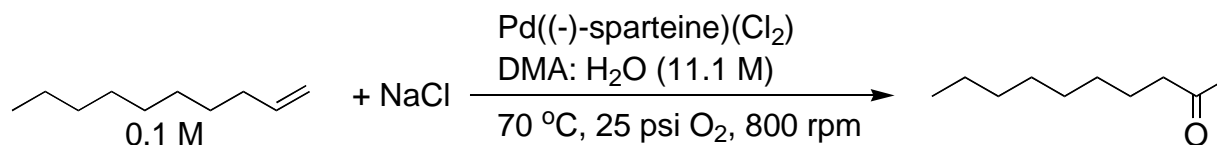
Water (x mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69  $\mu\text{L}$  of a 0.029M solution in DMA, 0.002 mmol), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi with O<sub>2</sub>, heated to 70  $^\circ\text{C}$ , and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene (114  $\mu\text{L}$ , 0.3 M) was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

[water]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
1.4	0.00194	2.00E-05
2.1	0.00167	1.00E-05
2.8	0.00209	2.00E-05
4.2	0.00539	7.00E-05
5.0 <sup>a</sup>	0.0086	1.82E-04
5.6	0.01147	1.90E-04
6.5	0.01586	2.60E-04
7.4 <sup>a</sup>	0.02237	5.29E-04

<sup>a</sup> average of 2 values



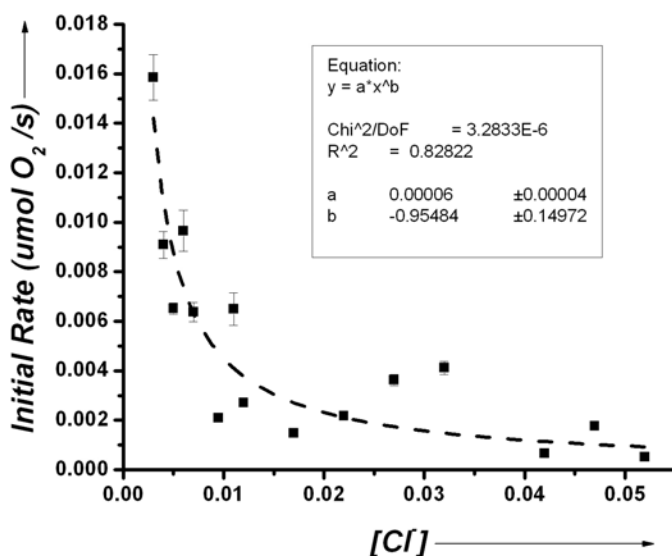
#### Chloride inhibition at low [decene] (0.1 M)



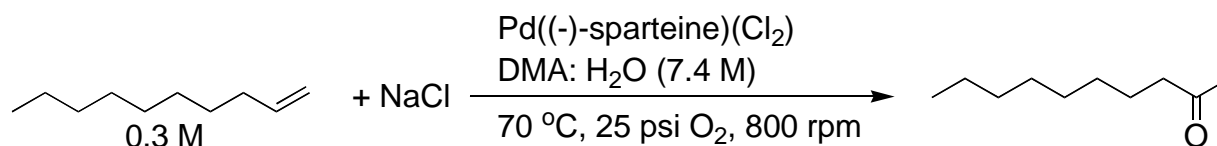
Water (total volume 0.40 mL, 11.1 M), NaCl (x  $\mu\text{L}$  of a 0.49 M solution in  $\text{H}_2\text{O}$ ), tetradecane (0.2 mL of a 0.1 M solution in DMA),  $\text{Pd((-)-sparteine)Cl}_2$  (69  $\mu\text{L}$  of a 0.029M solution in DMA, 0.002 mmol), and DMA (total volume 2.0 mL) were charged to a  $\text{O}_2$ -uptake reaction vessel. The solution was evacuated and filled with  $\text{O}_2$  five times before being pressurized to 25 psi with  $\text{O}_2$ , heated to 70  $^\circ\text{C}$ , and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene (38  $\mu\text{L}$ , 0.1 M) was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of  $\text{O}_2$  and the conversion of the reaction was monitored by consumption of  $\text{O}_2$  and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.



[NaCl]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
0.003	0.01585	9.20E-04
0.004	0.00909	5.40E-04
0.005	0.00651	2.30E-04
0.006	0.00965	8.30E-04
0.007	0.00637	3.80E-04
0.0095	0.00209	5.00E-05
0.011	0.00649	6.50E-04
0.012	0.00271	1.30E-04
0.017	0.00147	9.00E-05
0.022	0.00217	7.00E-05
0.027	0.00363	2.20E-04
0.032	0.00412	2.70E-04
0.042	6.60E-04	2.00E-05
0.047	0.00177	6.00E-05
0.052	5.10E-04	2.00E-05

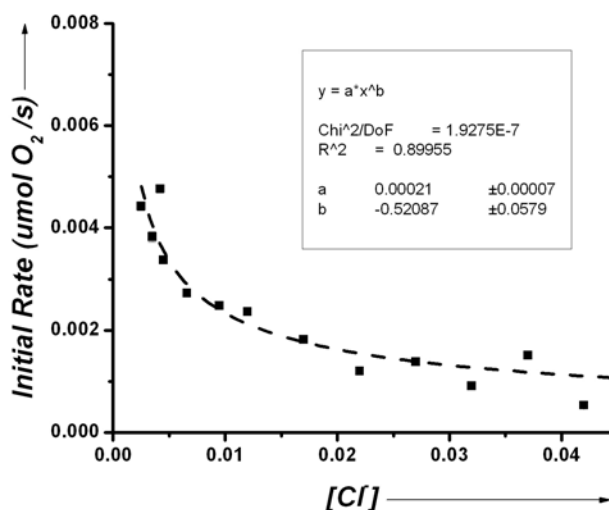


#### Chloride inhibition at high [decene] (0.3 M)

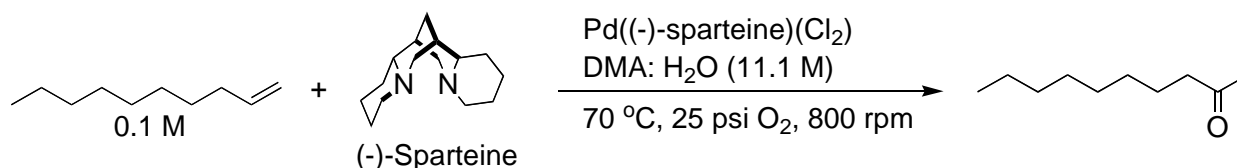


Water (total volume 0.27 mL, 7.4 M), NaCl (x  $\mu\text{L}$  of a 0.49 M solution in  $\text{H}_2\text{O}$ ), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine) $\text{Cl}_2$  (69  $\mu\text{L}$  of a 0.029M solution in DMA, 0.002 mmol), and DMA (total volume 2.0 mL) were charged to a  $\text{O}_2$ -uptake reaction vessel. The solution was evacuated and filled with  $\text{O}_2$  five times before being pressurized to 25 psi with  $\text{O}_2$ , heated to 70  $^\circ\text{C}$ , and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene (114  $\mu\text{L}$ , 0.3 M) was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of  $\text{O}_2$  and the conversion of the reaction was monitored by consumption of  $\text{O}_2$  and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

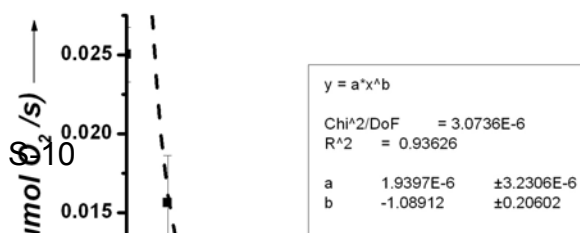
[NaCl]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
0.0042	0.00476	8.00E-05
0.0066	0.00273	5.00E-05
0.032	9.10E-04	1.00E-05
0.042	5.30E-04	9.34E-06
0.0025	0.00442	8.00E-05
0.0035	0.00382	1.00E-04
0.0045	0.00336	4.00E-05
0.012	0.00236	2.00E-05
0.017	0.00182	2.00E-05
0.022	0.0012	1.00E-05
0.027	0.00138	2.00E-05
0.037	0.00151	2.00E-05
0.047	0.00137	1.00E-05
0.0095	0.00248	2.00E-05



**(-)-Sparteine inhibition at low [decene] (0.1 M)**



Water (total volume 0.40 mL, 11.1 M), (–)-sparteine (x  $\mu\text{L}$ ), tetradecane (0.2 mL of a 0.1 M solution in DMA),  $\text{Pd}((-)\text{-sparteine})\text{Cl}_2$  (69  $\mu\text{L}$  of a 0.029M solution in DMA, 0.002 mmol), and DMA (total volume 2.0 mL) were charged to a  $\text{O}_2$ -uptake reaction vessel. The solution was evacuated and filled with  $\text{O}_2$  five times before being pressurized to 25 psi with  $\text{O}_2$ , heated to  $70^\circ\text{C}$ , and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene (38  $\mu\text{L}$ , 0.1 M) was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of  $\text{O}_2$  and the conversion of the reaction was monitored by consumption of  $\text{O}_2$  and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

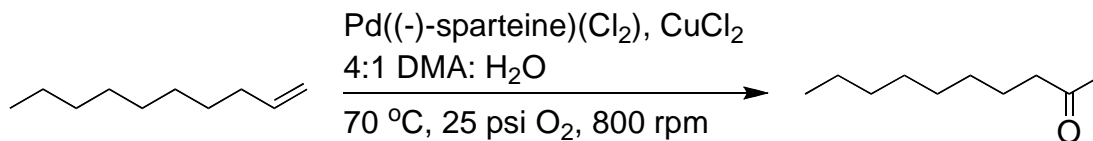


[sparteine]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
0.0003	0.01562	0.00298
0.0005	0.01010	0.00161
0.0010	0.00143	0.00007
0.0015	0.00279	0.00014
0.0020	0.00088	0.00007
0.0030	0.00055	0.00002

### Determination of $K_{D1}$

Water (total volume 0.40 mL, 11.1 M), Pd((-)-sparteine) $\text{Cl}_2$  (69  $\mu\text{L}$  of a 0.029M solution in DMA, 0.002 mmol), and DMA (total volume 2.0 mL) were heated to 70 °C and stirred for 15 minutes. The  $[\text{Cl}^-]$  was measured using a SympHony Chloride Electrode to be 0.001 M. The same  $[\text{Cl}^-]$  was measured when the  $[\text{H}_2\text{O}]$  was decreased to 7.4 M. From the error of the electrode (0.00005 M) the dissociation constant ( $K_{D1}$ ) can be determined to be greater than 0.018.

### Dependence on decene with 0.001 M $\text{CuCl}_2$

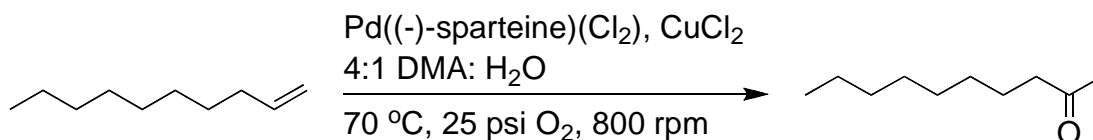


Water (0.333 mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine) $\text{Cl}_2$  (69  $\mu\text{L}$  of a 0.029M solution in DMA),  $\text{CuCl}_2$  (0.067 mL of a 0.03 M solution in water), and DMA (total volume 2.0 mL) were charged to a  $\text{O}_2$ -uptake reaction vessel. The

solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the pressure stabilized. Decene was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to μmol of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

[[decene]	Initial rate (μmol O <sub>2</sub> /s)	error
0.05	0.01221	9.30E-04
0.075	0.0282	0.00297
0.125	0.04747	0.00212
0.175	0.06205	0.0029
0.225	0.07896	0.00205

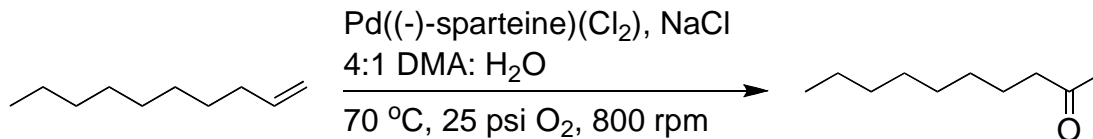
#### Dependence on decene with 0.01 M CuCl<sub>2</sub>



Water (0.19 mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69 μL of a 0.029M solution in DMA), CuCl<sub>2</sub> (0.08 mL of a 0.25 M solution in water), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the pressure stabilized. Decene was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to μmol of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

[[decene]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
0.1	6.80E-04	7.00E-05
0.15	0.00194	5.00E-05
0.2	0.00497	1.50E-04
0.25	0.00486	6.00E-05
0.3	0.00947	1.30E-04
0.125	0.0011	3.00E-05
0.175	0.00225	4.00E-05
0.275	0.00701	1.00E-04

### Dependence on decene with 0.01 M NaCl



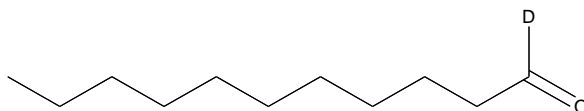
Water (0.19 mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69  $\mu\text{L}$  of a 0.029M solution in DMA), NaCl (0.08 mL of a 0.25 M solution in water), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the pressure stabilized. Decene was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu\text{mol}$  of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene.

[[decene]	Initial rate ( $\mu\text{mol O}_2/\text{s}$ )	error
0.05	0.00038	4.00E-05
0.1	0.00114	1.33E-07
0.15	0.00196	4.00E-05

0.2	0.002315	1.35E-07
0.25	0.00226	1.01E-07
0.3	0.00216	8.76E-08
0.35	0.00234	3.00E-05

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### Synthesis of 2-deutero-undec-1ene



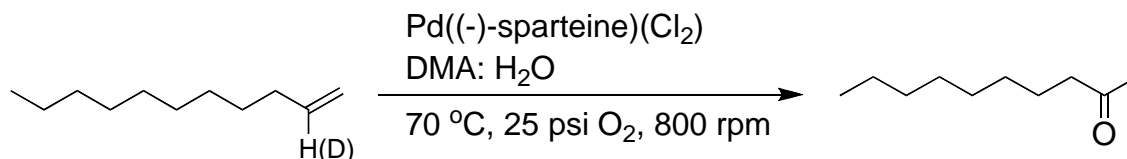
Methyl deconate (423 mg, 2.3 mmol) was added dropwise to a slurry of lithium aluminum deuteride (386 mg, 9.2 mmol) in 15 mL of THF at -78 °C. The slurry was allowed to warm to room temperature before being heated under reflux for 10 hours. The mixture was quenched by slow addition of 1 mL of H<sub>2</sub>O and the product was extracted with 50 mL of diethyl ether. The ether was washed with saturated NaHCO<sub>3</sub>, brine, dried with NaSO<sub>4</sub>, and concentrated *in vacuo* to give 365 mg (98%) of a colorless liquid.

The deuterated alcohol was then added dropwise to a solution of oxalyl chloride (388 µL, 4.5 mmol) and dimethyl sulfoxide (653 µL, 13.8 mmol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> at -78 °C. The mixture was stirred for 1 hour before triethyl amine (1.9 mL, 13.8 mmol) was added and the solution was allowed to warm to room temperature. The mixture was quenched with 5 mL of aqueous NH<sub>4</sub>Cl, extracted with 50 mL of ether, washed with brine, dried with MgSO<sub>4</sub>, and concentrated *in vacuo* to give 330 mg (91%) 1-*deutero*-decanal as a colorless liquid.

Methyltriphenylphosphonium bromide (787 mg, 2.1 mmol) in 15 mL of THF was treated with butyl lithium (840 µL of a 2.5 M solution in hexanes) at -78 °C. The mixture was allowed to warm to room temperature for 10 minutes before returning to -78 °C and treated with 1-*deutero*-decanal (330 mg, 2.1 mmol) and stirred for 1 hour before allowing to warm to room temperature. Silica (50 mg) was added to the slurry and the solution was decanted. The

remaining solid was washed with hexanes (3 x 30 mL), the organic fractions were combined and the solvent was removed to give an oil. The 2-deutero-undec-1-ene was purified by Kugelrohr distillation to give 250 mg (77%) of the desired product containing 93% deuterium incorporation as determined by GC-MS.

### Kinetics with 2-deutero-undec-1-ene

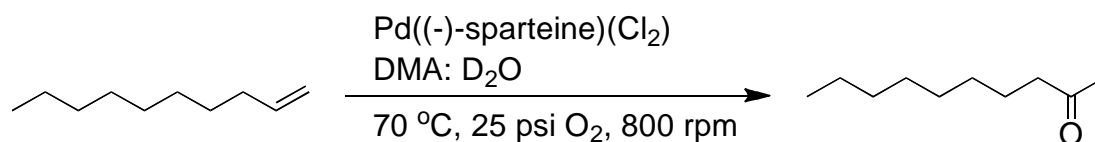


Water (0.4 mL), tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69  $\mu$ L of a 0.029M solution in DMA), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the pressure stabilized. Undecene was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to  $\mu$ mol of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of undecene. No KIE was observed at 0.1 M or 0.3 M undecene. The product, 2-undecanone, contained 60% deuterium incorporation as determined by GCMS.

[undecene]	Initial Rate	error	Initial Rate	error	kH/kD
0.1	0.0124	1.39708E-05	0.0122	3.70E-04	1.0
0.3	0.0067	1.73472E-06	0.0076	1.40E-04	0.9

### Kinetic Isotope Effect: $k_{H20}/k_{D20}$

The effect of D<sub>2</sub>O on the reaction rate was studied at both low and high [decene] reaction conditions.



D<sub>2</sub>O, tetradecane (0.2 mL of a 0.1 M solution in DMA), Pd((-)-sparteine)Cl<sub>2</sub> (69 μL of a 0.029M solution in DMA, 0.002 mmol), and DMA (total volume 2.0 mL) were charged to a O<sub>2</sub>-uptake reaction vessel. The solution was evacuated and filled with O<sub>2</sub> five times before being pressurized to 25 psi with O<sub>2</sub>, heated to 70 °C, and stirred at 800 rpm. The mixture was stirred for 20 minutes and the temperature and pressure stabilized. Decene was injected and the pressure was measured in each well every 5 seconds. The pressure was converted to μmol of O<sub>2</sub> and the conversion of the reaction was monitored by consumption of O<sub>2</sub> and was confirmed by GC. The initial rate of the reaction was determined for the first two percent conversion of decene. The average initial rates for reaction in D<sub>2</sub>O were compared to the average rates with H<sub>2</sub>O. At low [decene] a KIE of  $1.6 \pm 0.1$  was observed. At high concentration a KIE of  $2.6 \pm 0.1$  was observed. The data can be seen in the table below.

Table 1. Comparison of H<sub>2</sub>O to D<sub>2</sub>O

[decene]	D or H	initial rate (μmol O <sub>2</sub> /s)	error
0.1	D <sub>2</sub> O	0.00799	5.80E-04
0.1	D <sub>2</sub> O	0.00766	2.80E-04
0.1	D <sub>2</sub> O	0.00932	4.70E-04
0.1	H <sub>2</sub> O	0.0091	0.00102
0.1	H <sub>2</sub> O	0.01831	0.00137
0.1	H <sub>2</sub> O	0.01267	0.00113
0.3	D <sub>2</sub> O	0.00825	1.30E-04
0.3	D <sub>2</sub> O	0.00636	1.10E-04
0.3	D <sub>2</sub> O	0.00539	8.00E-05
0.3	H <sub>2</sub> O	0.02019	6.30E-04



0.3	H <sub>2</sub> O	0.01906	0.00158
0.3	H <sub>2</sub> O	0.01205	4.20E-04

Table 2. Kinetic isotope effect

Conditions		Average Initial Rate (μmol O <sub>2</sub> /s)	Error	k <sub>H</sub> /k <sub>D</sub>	error
<i>Low [decene]</i>	D <sub>2</sub> O	0.008323	0.000266	<b>1.6</b>	<b>0.1</b>
	H <sub>2</sub> O	0.013360	0.000683		
<i>high [decene]</i>	D <sub>2</sub> O	0.006667	0.000063	<b>2.6</b>	<b>0.1</b>
	H <sub>2</sub> O	0.017100	0.000584		

### RATE LAW DERIVATION



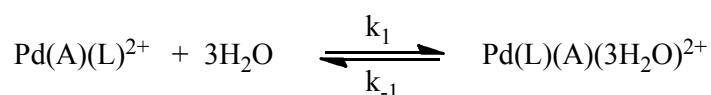
Pd = Pd((-)-sparteine)



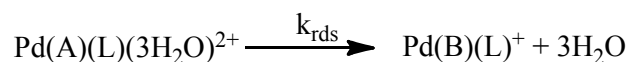
A = decene



B = -CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH(OH<sub>2</sub>)CH<sub>3</sub>



L = DMA



### Rate

$$v = k_{\text{rds}} [\text{Pd}(\text{A})(\text{L})(3\text{H}_2\text{O})^{2+}]$$

### Total Pd:

$$[\text{Pd}]_T = [\text{PdCl}_2] + [\text{Pd}(\text{L})(\text{Cl})^+] + [\text{PdL}_2^{2+}] + [\text{Pd}(\text{A})(\text{L})^{2+}] + [\text{Pd}(\text{A})(\text{L})(3\text{H}_2\text{O})^{2+}]$$

$$K_{D1} = \frac{[\text{Pd}(\text{Cl})(\text{L})^+][\text{Cl}^-]}{[\text{PdCl}_2][\text{L}]} \quad K_{D2} = \frac{[\text{PdL}_2^{2+}][\text{Cl}^-]}{[\text{Pd}(\text{Cl})(\text{L})^+][\text{L}]} \quad K_A = \frac{[\text{Pd}(\text{A})(\text{L})^{2+}][\text{L}]}{[\text{PdL}_2^{2+}][\text{A}]}$$

### SS assumption:

$$0 = k_1[Pd(A)(L)^{2+}][H_2O]^3 - k_{-1}[Pd(A)(L)(3H_2O)^{2+}] - k_{rds}[Pd(A)(L)(3H_2O)^{2+}]$$

**Rearrange  $K_{D1}$  expression:**

$$[PdCl_2] = \frac{[Pd(Cl)(L)^+][Cl^-]}{K_{D1}[L]}$$

**Sub into the expression for  $[Pd]_T$ :**

$$[Pd]_T = \frac{[Pd(Cl)(L)^+][Cl^-]}{K_{D1}[L]} + [Pd(L)(Cl)^+] + [PdL_2^{2+}] + [Pd(A)(L)^{2+}] + [Pd(A)(L)(3H_2O)^{2+}]$$

**Combine terms:**

$$[Pd]_T = [Pd(L)(Cl)^+] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} \right) + [PdL_2^{2+}] + [Pd(A)(L)^{2+}] + [Pd(A)(L)(3H_2O)^{2+}]$$

**Rearrange  $K_{D2}$  expression**

$$[Pd(Cl)(L)^+] = \frac{[PdL_2^{2+}][Cl^-]}{K_{D2}[L]}$$

**Sub into  $[Pd]_T$  expression:**

$$[Pd]_T = \frac{[PdL_2^{2+}][Cl^-]}{K_{D2}[L]} \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} \right) + [PdL_2^{2+}] + [Pd(A)(L)^{2+}] + [Pd(A)(L)(3H_2O)^{2+}]$$

**Rearrange, combine terms:**

$$[Pd]_T = \frac{[PdL_2^{2+}][Cl^-]}{K_{D2}[L]} \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} \right) + [Pd(A)(L)^{2+}] + [Pd(A)(L)(3H_2O)^{2+}]$$

**Rearrange  $K_A$  expression**

$$[PdL_2^{2+}] = \frac{[Pd(A)(L)^{2+}][L]}{K_A[A]}$$

**Sub into  $[Pd]_T$  expression:**

$$[Pd]_T = \frac{[Pd(A)(L)^{2+}][L][Cl^-]}{K_A K_{D2}[L][A]} \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} \right) + [Pd(A)(L)^{2+}] + [Pd(A)(L)(3H_2O)^{2+}]$$

**range, combine terms:**

$$[Pd]_T = \frac{[Pd(A)(L)^{2+}][Cl^-]}{K_A K_{D2}[A]} \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} \right) + [Pd(A)(L)(3H_2O)^{2+}]$$

**Rearrange SS assumption:**

$$0 = k_1[Pd(A)(L)^{2+}][H_2O]^3 - k_{-1}[Pd(A)(L)(3H_2O)^{2+}] - k_{rds}[Pd(A)(L)(3H_2O)^{2+}]$$

$$k_1[Pd(A)(L)^{2+}][H_2O]^3 = k_{-1}[Pd(A)(L)(3H_2O)^{2+}] + k_{rds}[Pd(A)(L)(3H_2O)^{2+}]$$

$$[Pd(A)(L)^{2+}] = \frac{[Pd(A)(L)(3H_2O)^{2+}](k_{-1} + k_{rds})}{k_1[H_2O]^3}$$

**Sub into [Pd]<sub>T</sub> expression:**

$$[Pd]_T = \frac{[Pd(A)(L)(3H_2O)^{2+}](k_{-1} + k_{rds})[Cl^-]}{k_1[H_2O]^3 K_A K_{D2}[A]} \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} \right) + [Pd(A)(L)(3H_2O)^{2+}]$$

**Combine terms:**

$$[Pd]_T = \frac{[Pd(A)(L)(3H_2O)^{2+}](k_{-1} + k_{rds})[Cl^-]}{k_1[H_2O]^3 K_A K_{D2}[A]} \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)$$

**Solve for [Pd(A)(L)(3H<sub>2</sub>O)<sup>2+</sup>]**

$$[Pd(A)(L)(3H_2O)^{2+}] = \frac{[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}$$

**Sub into rate expression:**

$$v = \frac{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}$$

**At high [A] expression simplifies to:**

$$v = \frac{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-] \left( \frac{K_A K_{D2}[A]}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}$$

$$v = \frac{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}}{(k_{-1} + k_{rds})[Cl^-] \left( \frac{K_A K_{D2}}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}}{(k_{-1} + k_{rds})[Cl^-]} \right)}$$

**Solve for Cl dependence  
inverse:**

$$\frac{1}{v} = \frac{(k_{-1} + k_{rds})[Cl^-] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]}$$

expand

$$\frac{1}{v} = \frac{\left( (k_{-1} + k_{rds})[Cl^-] + \frac{(k_{-1} + k_{rds})[Cl^-][Cl^-]}{K_{D1}[L]} + \frac{(k_{-1} + k_{rds})[Cl^-]K_{D2}[L]}{[Cl^-]} + \frac{(k_{-1} + k_{rds})[Cl^-]K_A K_{D2}[A]}{[Cl^-]} + \frac{(k_{-1} + k_{rds})[Cl^-]k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]}$$

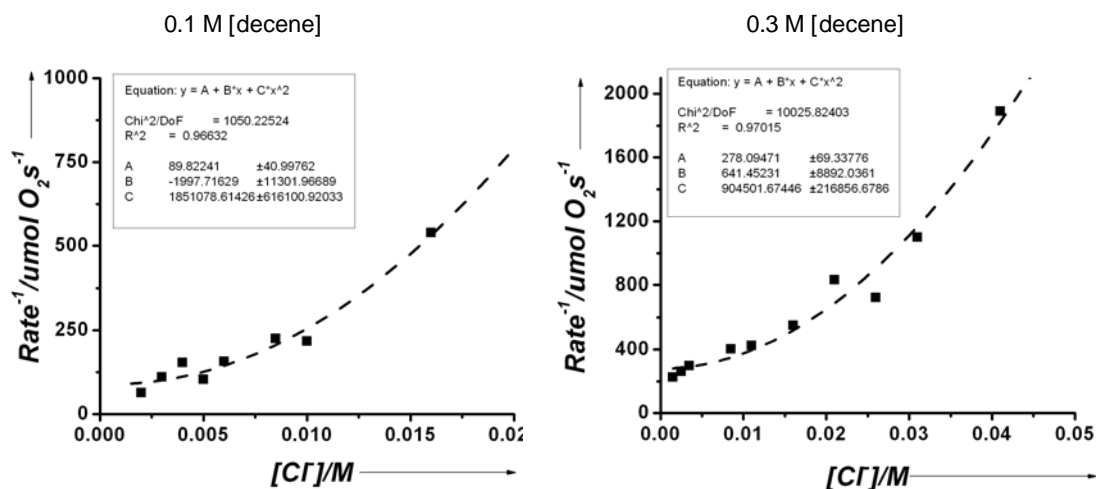
$$\frac{1}{v} = \frac{\left( (k_{-1} + k_{rds})[Cl^-] + \frac{(k_{-1} + k_{rds})[Cl^-]^2}{K_{D1}[L]} + (k_{-1} + k_{rds})K_{D2}[L] + (k_{-1} + k_{rds})K_A K_{D2}[A] + k_1[H_2O]^3 K_A K_{D2}[A] \right)}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]}$$

$$\frac{1}{v} = \frac{(k_{-1} + k_{rds})[Cl^-]}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]} + \frac{(k_{-1} + k_{rds})[Cl^-]^2}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]} + \frac{(k_{-1} + k_{rds})K_{D2}[L]}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]} + \frac{(k_{-1} + k_{rds})K_A K_{D2}[A]}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{k_{rds}[Pd]_T k_1[H_2O]^3 K_A K_{D2}[A]}$$

$$\frac{1}{v} = \frac{(k_{-1} + k_{rds})[Cl^-]}{k_{rds}k_1K_A K_{D2}[Pd]_T[H_2O]^3[A]} + \frac{(k_{-1} + k_{rds})[Cl^-]^2}{k_{rds}K_{D1}k_1K_A K_{D2}[Pd]_T[H_2O]^3[L][A]} + \frac{(k_{-1} + k_{rds})[L]}{k_{rds}k_1K_A[Pd]_T[H_2O]^3[A]} + \frac{(k_{-1} + k_{rds})}{k_{rds}k_1[Pd]_T[H_2O]^3} + \frac{1}{k_{rds}[Pd]_T}$$

$$\frac{1}{v} = \frac{(k_{-1} + k_{rds})[Cl^-]^2}{k_{rds}K_{D1}k_1K_A K_{D2}[Pd]_T[H_2O]^3[L][A]} + \frac{(k_{-1} + k_{rds})[Cl^-]}{k_{rds}k_1K_A K_{D2}[Pd]_T[H_2O]^3[A]} + \frac{(k_{-1} + k_{rds})[L]}{k_{rds}k_1K_A[Pd]_T[H_2O]^3[A]} + \frac{(k_{-1} + k_{rds})}{k_{rds}k_1[Pd]_T[H_2O]^3} + \frac{1}{k_{rds}[Pd]_T}$$

Fit to  $y = ax^2 + bx + c$



100 mM decene		300 mM decene	
[Cl <sup>-</sup> ]	Rate <sup>-1</sup> (μmol O <sub>2</sub> s <sup>-1</sup> )	[Cl <sup>-</sup> ]	Rate <sup>-1</sup> (μmol O <sub>2</sub> s <sup>-1</sup> )
0.002	63.1	0.031	1100
0.003	110.0	0.041	1890
0.004	153.6	0.0015	226
0.005	103.6	0.0025	262

0.006	157.0	0.0035	298
0.0085	225.2	0.011	424
0.01	217.4	0.016	549
0.016	539.1	0.021	833
		0.026	725
		0.0085	403

### Dependence on Alkene

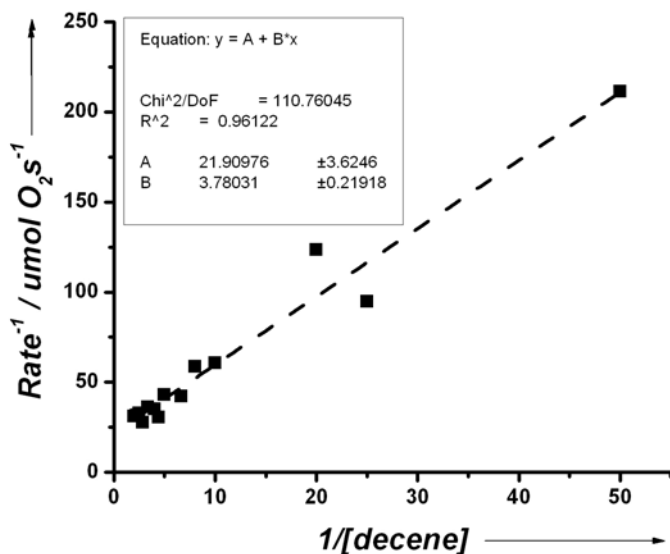
Solve for dependence on [A]:

$$v = \frac{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2} [A]}{(k_{-1} + k_{rds})[Cl^-] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2} [A]}{[Cl^-]} + \frac{k_1 [H_2O]^3 K_A K_{D2} [A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}$$

$$\frac{1}{v} = \frac{(k_{-1} + k_{rds})[Cl^-]}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2} [A]} + \frac{(k_{-1} + k_{rds})[Cl^-]^2}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2} [A] K_{D1} [L]} + \frac{(k_{-1} + k_{rds})[L]}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A [A]} + \frac{(k_{-1} + k_{rds})}{k_{rds}[Pd]_T k_1 [H_2O]^3} + \frac{1}{k_{rds}[Pd]_T}$$

$$\frac{1}{v} = \frac{1}{[A]} \left( \frac{(k_{-1} + k_{rds})[Cl^-]}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2}} + \frac{(k_{-1} + k_{rds})[Cl^-]^2}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2} K_{D1} [L]} + \frac{(k_{-1} + k_{rds})[L]}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A} \right) + \frac{(k_{-1} + k_{rds})}{k_{rds}[Pd]_T k_1 [H_2O]^3} + \frac{1}{k_{rds}[Pd]_T}$$

Fit  $y = mx + b$



$[decene]^{-1}$	$Rate^{-1}$ ( $\mu mol O_2 s^{-1}$ )
50.00	211.4
25.00	94.8
20.00	123.6
10.00	60.6
8.00	58.7
6.67	42.2
5.00	43.0
4.44	30.3
4.00	35.1
3.33	36.1
2.86	27.6
2.50	32.7
2.22	31.6
2.00	31.1

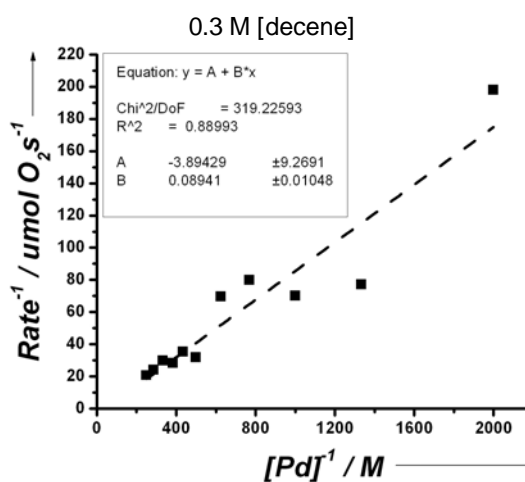
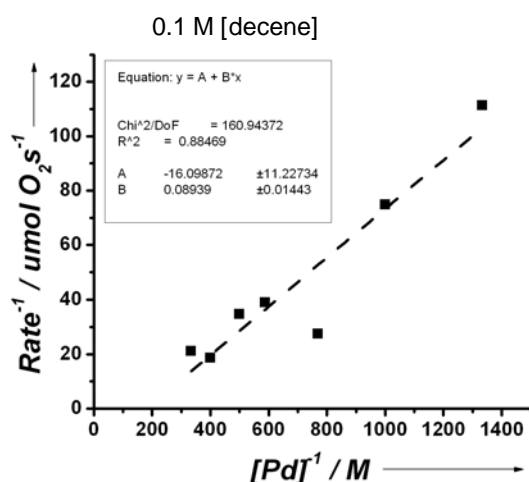
### Pd dependence

$$\frac{1}{v} = \frac{(k_{-1} + k_{rds})[Cl^-] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2} [A]}{[Cl^-]} + \frac{k_1 [H_2O]^3 K_A K_{D2} [A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2} [A]}$$

$$\frac{1}{v} = \left( \frac{1}{[Pd]_T} \right) \frac{(k_{-1} + k_{rds})[Cl^-] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)}{k_{rds} k_1 [H_2O]^3 K_A K_{D2}[A]}$$

$$y = mx$$

$$v = \left( \frac{k_{rds} k_1 [H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-] \left( 1 + \frac{[Cl^-]}{K_{D1}[L]} + \frac{K_{D2}[L]}{[Cl^-]} + \frac{K_A K_{D2}[A]}{[Cl^-]} + \frac{k_1[H_2O]^3 K_A K_{D2}[A]}{(k_{-1} + k_{rds})[Cl^-]} \right)} \right) [Pd]_T$$



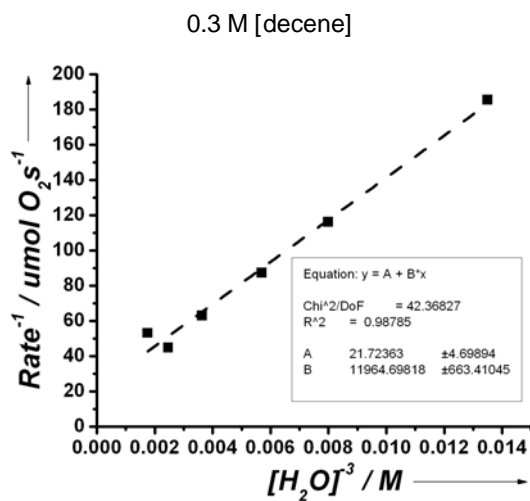
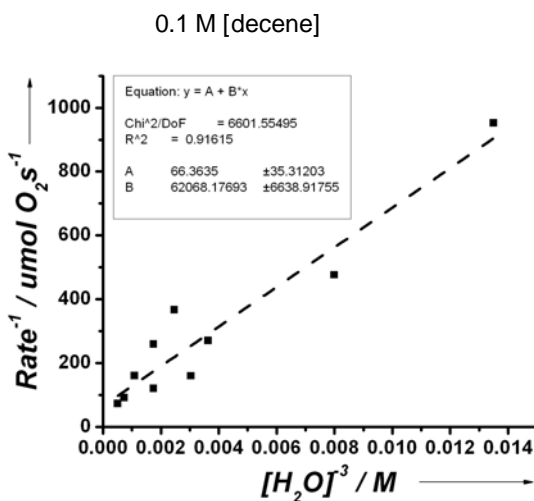
100 mM decene		300 mM decene	
$[Pd]^{-1}$	$\text{Rate}^{-1}$ ( $\mu\text{mol O}_2\text{s}^{-1}$ )	$[Pd]^{-1}$	$\text{Rate}^{-1}$ ( $\mu\text{mol O}_2\text{s}^{-1}$ )
1333	111.4	2000.0	198.0
1000	74.9	1333.3	77.2
769	27.5	1000.0	70.2
588	39.1	769.2	79.9
500	34.8	625.0	69.7
400	18.6	500.0	31.8
333	21.2	434.8	35.3
		384.6	28.2
		333.3	29.9
		285.7	24.1
		250.0	20.7

### Solve for dependence of water:

$$\frac{1}{v} = \frac{(k_{-1} + k_{rds})[Cl^-]}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2}[A]} + \frac{(k_{-1} + k_{rds})[Cl^-]^2}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A K_{D2}[A] K_{D1}[L]} + \frac{(k_{-1} + k_{rds})[L]}{k_{rds}[Pd]_T k_1 [H_2O]^3 K_A [A]} + \frac{(k_{-1} + k_{rds})}{k_{rds}[Pd]_T k_1 [H_2O]^3} + \frac{1}{k_{rds}[Pd]_T}$$

$$\frac{1}{v} = \frac{1}{[H_2O]^3} \left( \frac{(k_{-1} + k_{rds})[Cl^-]}{k_{rds}[Pd]_T k_1 K_A K_{D2}[A]} + \frac{(k_{-1} + k_{rds})[Cl^-]^2}{k_{rds}[Pd]_T k_1 K_A K_{D2}[A] K_{D1}[L]} + \frac{(k_{-1} + k_{rds})[L]}{k_{rds}[Pd]_T k_1 K_A [A]} + \frac{(k_{-1} + k_{rds})}{k_{rds}[Pd]_T k_1} \right) + \frac{1}{k_{rds}[Pd]_T}$$

$$y = mx + b$$



100 mM decene		300 mM decene	
[water] <sup>-3</sup>	Rate <sup>-1</sup> (μmol O <sub>2</sub> s <sup>-1</sup> )	[water] <sup>-3</sup>	Rate <sup>-1</sup> (μmol O <sub>2</sub> s <sup>-1</sup> )
0.0135	952	0.0135	186
0.0080	476	0.0080	116
0.0036	270	0.0057	87
0.0030	160	0.0036	63
0.0025	366	0.0025	45
0.0018	120	0.0018	53
0.0018	259		
0.0011	160		
0.0007	92		
0.0005	72		

Theoretical details:

1. Methods
2. Solvation discussion
3. Coordinates

## 1. Methods:

All calculations were carried out with Jaguar version 7.5. Molecular geometries using the B3LYP exchange correlation functional were first optimized with a mixed basis set whereby the Pd atom was assigned the LACVP pseudopotential, adjacent atoms were assigned the 6-31G\* basis set, and the rest of the atoms were assigned the “midi!” basis set. After geometric convergence was obtained, the geometries were further optimized by assigning the 6-31G\*\* basis set to all atoms previously assigned with the midi! basis set. Vibrational frequencies at this level confirmed stationary intermediates with the correct number of imaginary frequencies. Finally, single point energy calculations at the B3LYP/LACV3P\*\*++ level yielded final electronic energies.

Solvation was treated with Jaguar’s implicit Poisson-Boltzmann continuum solver at the B3LYP/LACVP\*\* level. Dielectric constants ( $\epsilon_{\text{H}_2\text{O}} = 80.4$ ,  $\epsilon_{\text{DMA}} = 37.8$ ) and probe radii ( $r_{\text{H}_2\text{O}} = 1.40$ ,  $r_{\text{DMA}} = 2.64$ ) were used.

## 2. Solvation discussion:

The simulation of reactions in mixed solvents is difficult due to poorly defined thermal behavior of mixed solvents and the net dielectric effect of mixed solvents. We do not predict the actual solvation energy of a mixed solvent though we do report solvation energies of simulations in pure H<sub>2</sub>O and DMA solvents. Calculated energy differences are quite small regardless of the solvent selected, and total energies were small regardless if the molecular geometries were optimized in solvent or not. Thus, calculation data reported in the text are gas-phase optimized structures with single point solvation energy corrections, and we deem our values as quite reasonable approximations of the solvation energies of these species.



**Pd[(-)-sparteine]Cl<sub>2</sub>**

Gas phase energies (LACV3P\*\*++)

Gas phase : -1744.240885 a.u.

H<sub>2</sub>O optimized : -1744.238332 a. u.

DMA optimized : -1744.238723 a. u.

H<sub>2</sub>O solvation energies (LACVP\*\*)

Gas phase geometry : -0.033724938 a. u.

H<sub>2</sub>O optimized : -0.03833505039 a. u.

DMA solvation energies (LACVP\*\*)

Gas phase geometry : -0.035398414 a. u.

DMA optimized : -0.04022977438 a. u.

**Pd[(-)-sparteine](H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>**

Gas phase energies (LACV3P\*\*++)

Gas phase : -976.109154

H<sub>2</sub>O optimized : -976.10413320999

DMA optimized : -976.10520076782

H<sub>2</sub>O solvation energies (LACVP\*\*)

Gas phase geometry / H<sub>2</sub>O solvation : -0.257138753 a. u.

H<sub>2</sub>O optimized / H<sub>2</sub>O solvation : -0.26364721213 a. u.

DMA solvation energies (LACVP\*\*)

Gas phase geometry / DMA solvation : -0.255419769 a. u.

DMA optimized / DMA solvation: -0.25834512854 a. u.

**Pd[(-)-sparteine](DMA)<sub>2</sub><sup>2+</sup>**

Gas phase energies (LACV3P\*\*++)

Gas phase : -1399.094169 a. u.

H<sub>2</sub>O optimized : -1399.09390155332 a. u.

DMA optimized : -1399.09386782461 a. u.

H<sub>2</sub>O solvation energies (LACVP\*\*)

Gas phase geometry : -0.202726037 a. u.

H<sub>2</sub>O optimized : -0.20305161929 a. u.

DMA solvation energies (LACVP\*\*)

Gas phase geometry : -0.203105681 a. u.

DMA optimized : -0.20296511494 a. u.

### 3. Coordinates:

#### **PdCl2** nucleophilic attack transition state:

Atom	x	y	z	nbo_charge
Pd	0.0309	0.0625	0.0208	0.5560
C	0.2902	-0.0103	2.5861	-0.2003
O	0.9924	-0.1129	4.3243	-0.8400
C	1.3205	-0.2476	1.6153	-0.5868
H	1.6524	0.6714	4.3727	0.5381
Cl	-0.4881	-2.2386	-0.0794	-0.6261
H	1.6735	-1.2731	1.5236	0.2579
H	2.0973	0.5100	1.5453	0.2468
Cl	0.4982	2.4059	-0.0086	-0.6246
H	-0.0600	1.0057	2.7321	0.2638
H	-0.4536	-0.7818	2.7519	0.2731
H	1.5282	-0.9203	4.3413	0.5465
O	-1.3109	0.2139	-1.7493	-0.9615
H	-0.8132	0.5870	-2.4904	0.5504
H	-1.4126	-0.7392	-1.9199	0.5413
H	2.7526	2.2542	3.4600	0.5295
O	2.6341	1.8410	4.3601	-1.0178
H	2.3976	2.5643	4.9536	0.5297
H	2.0874	2.8710	1.3683	0.5085
O	2.8542	2.9708	1.9772	-1.0131
H	3.6328	2.8206	1.4276	0.5287

#### **Pd[(-)-sparteine]** nucleophilic attack transition state:

Atom	x	y	z	nbo_charge
Pd	-0.1586	-0.0221	0.0931	0.7536
C	-0.4823	-0.5807	2.7115	-0.2121
O	-0.1228	-0.8203	4.6699	-0.8922
H	0.8703	-0.6948	4.7417	0.5348
H	-1.5462	-0.4475	2.8837	0.2578
C	0.3009	0.4635	2.1801	-0.6629
H	-0.5349	-0.1177	5.1950	0.5335
H	1.3749	0.3176	2.2033	0.2544
H	-0.1721	-1.6083	2.5743	0.2630
H	0.0018	1.4831	2.3951	0.2529
O	2.5077	-0.5374	4.6326	-1.0168
H	2.8777	0.2308	5.0877	0.5237
H	3.0090	-1.3182	4.9721	0.5277
O	3.8874	-2.7449	5.4070	-1.0013
H	4.8159	-2.6634	5.6655	0.5335
H	3.4947	-3.3417	6.0592	0.5280
N	-1.7999	1.3582	-0.1933	-0.4680
C	-3.0061	0.4756	-0.5383	-0.0672
C	-4.3737	1.1876	-0.3824	-0.4834
C	-4.5453	1.9244	0.9473	-0.4697
C	-3.3868	2.9057	1.1230	-0.4870
C	-2.0588	2.1448	1.0722	-0.2661
C	-2.8713	-0.1174	-1.9613	-0.2893
H	-2.9720	-0.3360	0.1991	0.2654
H	-5.1402	0.4134	-0.4999	0.2692
H	-4.5298	1.8996	-1.1986	0.2465
H	-4.5597	1.2113	1.7832	0.2378
H	-5.5075	2.4444	0.9638	0.2615
H	-3.4299	3.4084	2.0959	0.2678
H	-3.4318	3.6991	0.3683	0.2477
H	-2.0656	1.4286	1.8940	0.2361
H	-1.2076	2.8167	1.2055	0.2676
C	-1.4538	2.3273	-1.2953	-0.2778
C	-1.4027	1.7108	-2.6993	-0.2857
C	-2.7295	1.0036	-3.0036	-0.4720
H	-3.7910	-0.6864	-2.1392	0.2960
C	-1.7163	-1.1116	-2.1545	-0.2729
H	-0.5045	2.7940	-1.0199	0.2676
H	-2.2112	3.1183	-1.3051	0.2634
C	-0.2472	0.7284	-2.9500	-0.0671
H	-1.2544	2.5472	-3.3921	0.2960

H	-2.7162	0.5823	-4.0142	0.2635
H	-3.5684	1.7027	-2.9725	0.2589
N	-0.3550	-0.4874	-2.0627	-0.5014
C	0.6588	-1.5045	-2.5161	-0.2704
H	-1.8230	-1.5664	-3.1499	0.2586
H	-1.7554	-1.9254	-1.4225	0.2615
C	1.1576	1.3368	-2.8833	-0.4766
H	-0.3884	0.3592	-3.9792	0.2598
C	2.0904	-0.9687	-2.5759	-0.4757
H	0.3489	-1.8359	-3.5178	0.2442
H	0.5886	-2.3610	-1.8437	0.2626
C	2.1998	0.3291	-3.3836	-0.4666
H	1.3917	1.6443	-1.8543	0.2371
H	1.1707	2.2440	-3.4974	0.2674
H	2.7215	-1.7530	-3.0086	0.2653
H	2.4541	-0.7913	-1.5609	0.2298
H	2.0276	0.1276	-4.4485	0.2420
H	3.2094	0.7438	-3.3041	0.2560
H	1.5146	-4.7392	2.1841	0.2500
H	1.9357	-5.0300	0.4823	0.2513
C	1.6025	-4.2723	1.1983	-0.4956
H	4.1051	-4.5875	1.5533	0.2559
H	0.6362	-3.8822	0.8892	0.2611
H	4.6882	-2.9265	1.4489	0.2566
C	3.8878	-3.5551	1.8353	-0.5007
N	2.5853	-3.1828	1.2618	-0.4101
H	3.8638	-3.4819	2.9288	0.2575
C	2.2760	-1.9397	0.8781	0.7247
O	1.1176	-1.7035	0.4045	-0.7058
H	4.2289	-1.1054	0.4609	0.2831
C	3.3199	-0.8551	1.0155	-0.7948
H	3.5918	-0.7141	2.0670	0.2872
H	2.9267	0.0804	0.6202	0.2694

**Pd[(-)-sparteine]Cl<sub>2</sub>**

Pd	-1.53852	0.22689	0.36338
N	-3.63748	1.00742	0.24462
C	-3.57937	2.26336	1.09377
C	-4.75818	3.24178	0.85920
C	-5.01235	3.54416	-0.62016
C	-5.20489	2.22623	-1.37324
C	-3.96915	1.34303	-1.18313
C	-3.46553	1.92325	2.60160
H	-2.66258	2.77137	0.77162
H	-4.52754	4.16184	1.41001
H	-5.68095	2.84423	1.29738
H	-4.15681	4.08533	-1.04637
H	-5.88620	4.19692	-0.72545
H	-5.32180	2.39916	-2.44929
H	-6.12509	1.72879	-1.03862
H	-3.09859	1.84836	-1.60104
H	-4.05105	0.39648	-1.72085
C	-4.60367	-0.00736	0.75633
C	-4.47669	-0.28838	2.25973
C	-4.63302	1.02389	3.03746
H	-3.50800	2.88123	3.13453
C	-2.15356	1.25411	3.04643
H	-4.44982	-0.91509	0.16681
H	-5.63281	0.32878	0.56886
C	-3.17891	-0.98030	2.71196
H	-5.29183	-0.97676	2.51638
H	-4.58724	0.83968	4.11738
H	-5.60407	1.48623	2.83778
N	-1.95812	-0.12349	2.50134
C	-0.81904	-0.76690	3.24365
H	-2.16565	1.19999	4.14746
H	-1.27942	1.84331	2.75501
C	-2.95831	-2.38245	2.13159
H	-3.27958	-1.09639	3.80611
C	-0.54769	-2.20795	2.80831

H	-1.07992	-0.73586	4.31439
H	0.06742	-0.15499	3.07710
Cl	0.78766	-0.04794	0.60275
Cl	-1.10537	0.40281	-1.93933
C	-1.80434	-3.08351	2.85990
H	-2.73581	-2.31148	1.05971
H	-3.88936	-2.95324	2.23693
H	0.23487	-2.61105	3.46208
H	-0.13574	-2.19075	1.79627
H	-2.09844	-3.26916	3.90306
H	-1.60482	-4.06216	2.41008

**Pd[(-)-sparteine](H<sub>2</sub>O)<sub>2</sub>**

Pd	-1.79456	0.02749	0.29690
N	-3.48435	1.27319	0.41292
C	-3.06981	2.50499	1.22085
C	-4.06488	3.68172	1.04974
C	-4.35285	4.02438	-0.41471
C	-4.83454	2.77693	-1.15665
C	-3.79886	1.65217	-1.01706
C	-2.87194	2.13410	2.70674
H	-2.11213	2.81516	0.78420
H	-3.62204	4.53865	1.56887
H	-5.00650	3.46342	1.56264
H	-3.45021	4.42044	-0.89815
H	-5.10599	4.81606	-0.46571
H	-4.95156	2.96944	-2.22856
H	-5.81726	2.45372	-0.79559
H	-4.11412	0.74030	-1.53063
H	-2.86010	2.01108	-1.44935
C	-4.62949	0.52334	1.03486
C	-4.40559	0.21321	2.52054
C	-4.15312	1.51672	3.29220
H	-2.62235	3.06454	3.22859
C	-1.69967	1.17539	2.96043
H	-4.79065	-0.37747	0.43737
H	-5.52861	1.14074	0.94165
C	-3.25820	-0.77211	2.80366
H	-5.32185	-0.26802	2.87983
H	-5.00527	2.19525	3.21212
H	-4.02362	1.31270	4.36003
N	-1.91629	-0.19634	2.37526
C	-0.81110	-1.11891	2.84853
H	-1.57062	1.05768	4.04384
H	-0.75744	1.56161	2.55896
C	-3.45708	-2.19589	2.27128
H	-3.18343	-0.84145	3.89964
C	-0.98439	-2.57639	2.41146
H	-0.81941	-1.06666	3.94484
H	0.13757	-0.69171	2.51580
O	0.23067	-0.90114	-0.12035
O	-1.60044	-0.10966	-1.89393
C	-2.36050	-3.13228	2.79222
H	-3.46942	-2.20278	1.17226
H	-4.44390	-2.54041	2.59790
H	-0.18075	-3.15816	2.87539
H	-0.86316	-2.67818	1.32507
H	-2.48727	-4.13901	2.38505
H	-2.43837	-3.22236	3.88278
H	-1.86011	0.49313	-2.60413
H	-0.74779	-0.50514	-2.13102
H	0.46145	-1.81001	0.12626
H	1.01495	-0.35725	0.05158

**Pd[(-)-sparteine](DMA)<sub>2</sub>**

Pd	-1.96082	-0.08441	0.29730
N	-3.90676	0.77185	0.50874
C	-3.70232	2.27547	0.68039
C	-4.99434	3.09927	0.45723

C	-5.71424	2.75978	-0.85113
C	-5.99016	1.25558	-0.90563
C	-4.67647	0.48076	-0.76039
C	-3.07301	2.57981	2.05838
H	-2.99531	2.55130	-0.11229
H	-4.70138	4.15501	0.47796
H	-5.68950	2.95775	1.29055
H	-5.09860	3.05556	-1.71163
H	-6.64471	3.33080	-0.92155
H	-6.42857	0.96662	-1.86723
H	-6.71949	0.96584	-0.14042
H	-4.82477	-0.60046	-0.80389
H	-4.02359	0.75673	-1.58766
C	-4.60655	0.14445	1.68284
C	-3.99688	0.52113	3.03952
C	-3.96746	2.04849	3.19064
H	-2.98252	3.67009	2.12417
C	-1.65229	2.02624	2.25172
H	-4.60332	-0.93608	1.51695
H	-5.65215	0.46928	1.67769
C	-2.58424	-0.02931	3.29662
H	-4.64503	0.07873	3.80443
H	-4.97382	2.47124	3.14829
H	-3.55611	2.32992	4.16579
N	-1.58229	0.52067	2.30086
C	-0.19124	0.12814	2.75276
H	-1.26174	2.41018	3.20341
H	-0.97130	2.36032	1.46255
C	-2.47518	-1.55167	3.41942
H	-2.27378	0.39134	4.26607
C	-0.01081	-1.36936	3.01010
H	-0.00590	0.68434	3.68139
H	0.51036	0.48702	1.99865
O	0.05373	-0.64106	-0.06588
O	-2.29177	-0.79664	-1.67855
C	-1.08669	-1.94745	3.93536
H	-2.67357	-2.03087	2.45095
H	-3.25554	-1.89417	4.10770
H	0.98851	-1.50797	3.43752
H	-0.02596	-1.90779	2.06008
H	-0.99173	-3.03583	3.99480
H	-0.95598	-1.56637	4.95603
C	-1.79129	-0.40341	-2.78252
C	-1.00434	0.88596	-2.87054
N	-1.98947	-1.13319	-3.88479
C	-2.76164	-2.38286	-3.84480
C	-1.52062	-0.75752	-5.22501
H	-1.54746	1.63231	-3.46032
H	-0.02898	0.73918	-3.34160
H	-0.84654	1.27808	-1.86681
H	-2.18971	-3.17368	-4.33854
H	-3.70651	-2.25239	-4.38194
H	-2.96590	-2.66072	-2.81430
H	-1.04022	0.21724	-5.22782
H	-2.37371	-0.72708	-5.90936
H	-0.81105	-1.50618	-5.59119
C	0.55059	-1.73232	-0.50061
C	-0.25263	-3.01393	-0.51166
N	1.81608	-1.74164	-0.93116
C	2.53822	-2.94724	-1.35834
C	2.63572	-0.52203	-0.91545
H	3.15337	-0.42833	-1.87392
H	3.38627	-0.58576	-0.12081
H	2.00512	0.34744	-0.74940
H	1.90256	-3.82827	-1.33797
H	3.39221	-3.11519	-0.69461
H	2.91421	-2.80454	-2.37587
H	0.17555	-3.74520	0.18199
H	-0.27297	-3.47208	-1.50414
H	-1.27607	-2.79994	-0.20925



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<sup>i</sup> S. K. Mandal, D. R. Jensen, J. S. Pugsley, M. S. Sigman, *J. Org. Chem.* **2003**, 68, 4600.