

Ethylene oxidation by a Pt(II) hydroxo complex. Insights into the Wacker Process

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Table S1. Variable temperature ^1H and ^{195}Pt NMR data for ethylene reaction of **4**.

Entry and Description		Temp	^1H NMR (δ) ^a	^{195}Pt NMR (δ)
1	1 h after C_2H_4 addition (yield of 6+7 = 10%)	RT	1.52 (br)	-2762 (4), -3081 (10), -3416 (10)
		0 °C	1.81 (br), 11.4 ^b	-2775 (4), -3092 (10), -3424 (10)
		-50 °C	4.07 (br), ^c 11.4 ^b	-2806 (4), -3110 (10), -3441 (10)
2	Maximum 10 (yield of 6+7 = 33%)	RT	2.11 (br), 11.4 ^b	-3080 (10), -3415 (10), -3872 (7)
		-20 °C	3.62 (br), 11.4 ^b	-3099 (10), -3431 (10), -3504 (13), -3909 (7)
		-50 °C	4.07 (br), ^c 11.4 ^b	-3110 (10), -3441 (10), -3541 (13), -3929 (7)
3	~3/4 th complete reaction (yield of 6+7 = 70%)	RT	11.4 ^b	-3081 (10), -3416 (10), -3471 (6), -3872 (7)
		-20 °C	4.15 ^b , 11.4 ^b	-3100 (10), -3433 (10), -3501 (13), -3909 (7)
		-50 °C	6.62 ^b , 11.4 ^b	-3111 (10), -3443 (10), -3539 (13), -3929 (7)
4	Reaction complete	RT		-3471 (6), -3872 (7)

^a Only ^1H NMR signals additional to those of **6-11** are listed.^b Weak unresolved signal.^c Overlaps with methylene signal of **7** at δ 3.97.

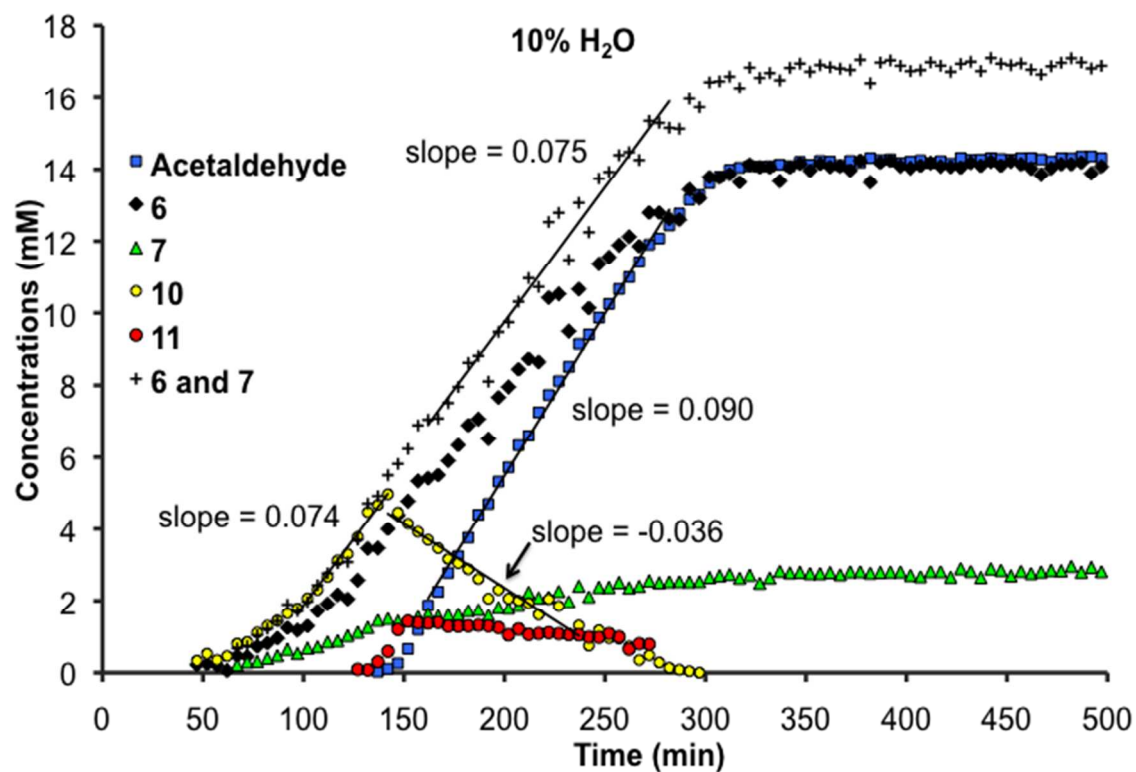


Figure S1. Ethylene reaction profile for [Pt(COD)(OH)]₂[OTf]₂ (**4**) in CD₂Cl₂ at 27 °C with 10% H₂O, ([**4**] = 9 mM, [C₂H₄] = 200 mM). Slopes are from least squares fits to linear portions of the plots.

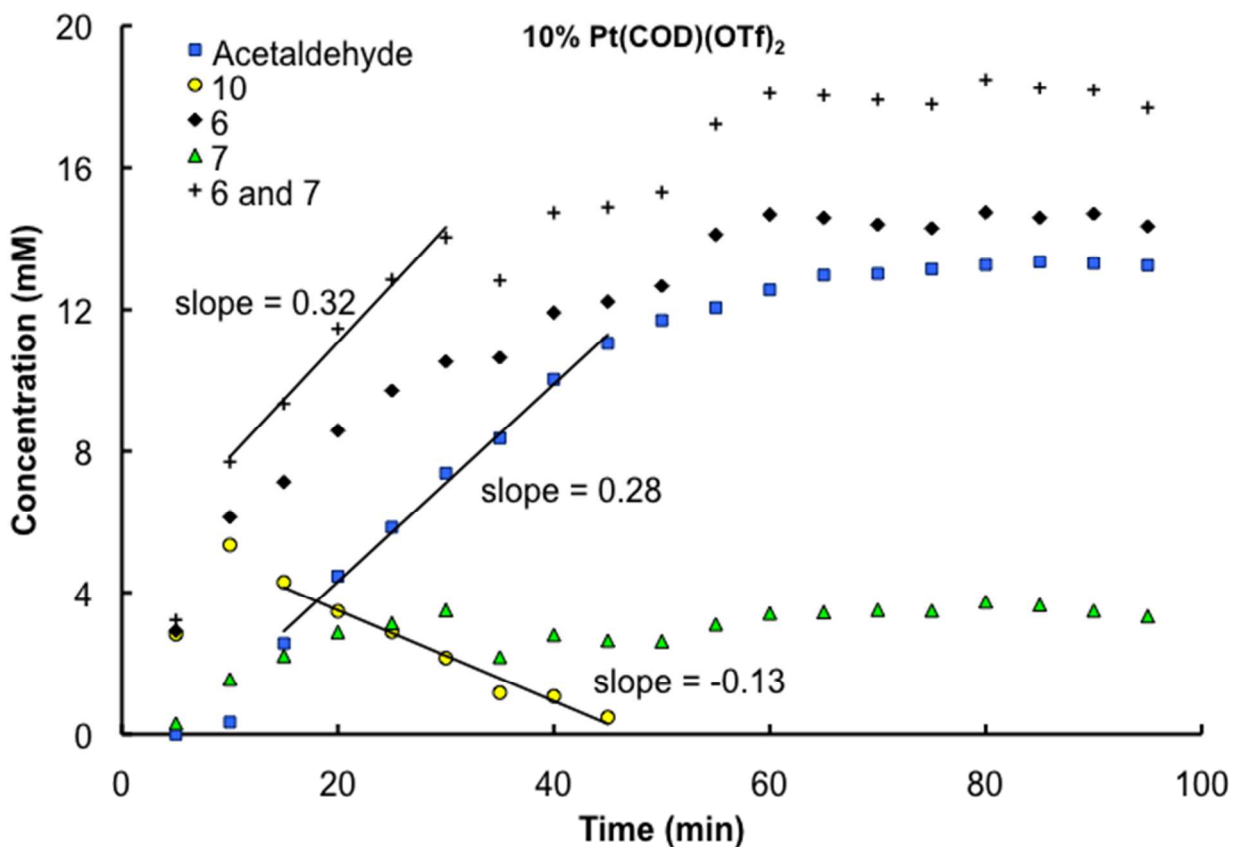


Figure S2. Ethylene reaction profile for [Pt(COD)(OH)]₂[OTf]₂ (**4**) in CD₂Cl₂ at 27 °C with 10% Pt(COD)(OTf)₂, ([**4**] = 9 mM, [C₂H₄] = 200 mM). Slopes are from least squares fits to linear portions of the plots.

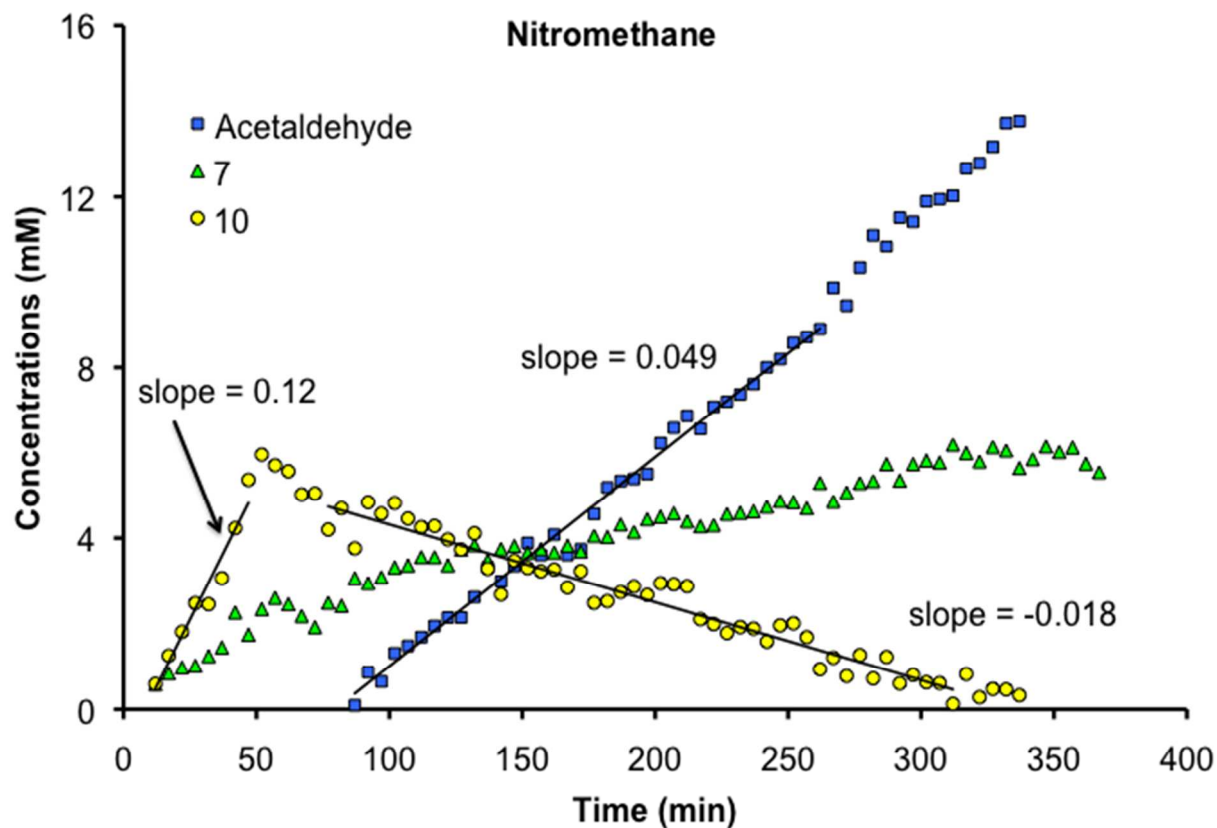


Figure S3. Ethylene reaction profile for $[\text{Pt}(\text{COD})(\text{OH})]_2[\text{OTf}]_2$ (**4**) in CD_3NO_2 at 27°C ($[\text{4}] = 9 \text{ mM}$, $[\text{C}_2\text{H}_4] \sim 200 \text{ mM}$). Slopes are from least squares fits to linear portions of the plots.

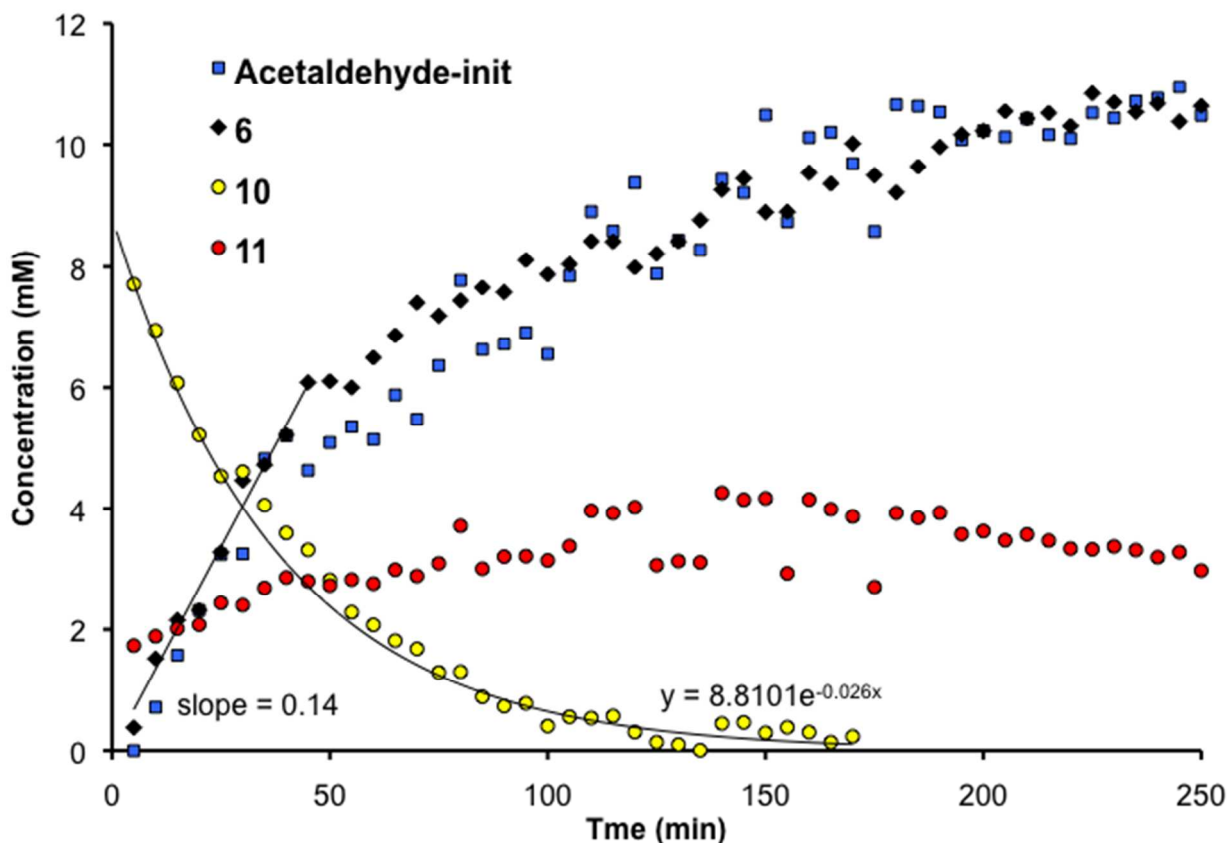


Figure S4. Ethylene reaction profile for a 10:1 mixture of 10 and 11 (prepared in situ from 4 (~9 mM) and vinyloxy-trimethylsilane) in CD_2Cl_2 at 27 °C with 10% HOTf and $[\text{C}_2\text{H}_4] = 200 \text{ mM}$. Acetaldehyde from the preparation of 10 has been subtracted.

Kinetic fitting and simulations of phases 1 and 2 used the Copasi program.¹ Ethylene was not included as a parameter as its concentration is constant (excess).

Abbreviations:

BT = $\text{Pt}(\text{COD})(\text{OTf})_2$

C = catalyst = H^+

CA = $[\text{Pt}(\text{COD})(\text{OH}_2)(\text{OTf})]^+$

W = water

ET = 6

AA = 4

A = $\text{Pt}(\text{COD})(\text{OH})(\text{OTf})$

V = 23

I = 10

EH = $\text{Pt}(\text{COD})(\text{OH})(\text{Et})$

A) Acidic coordinated water model with fitting parameters

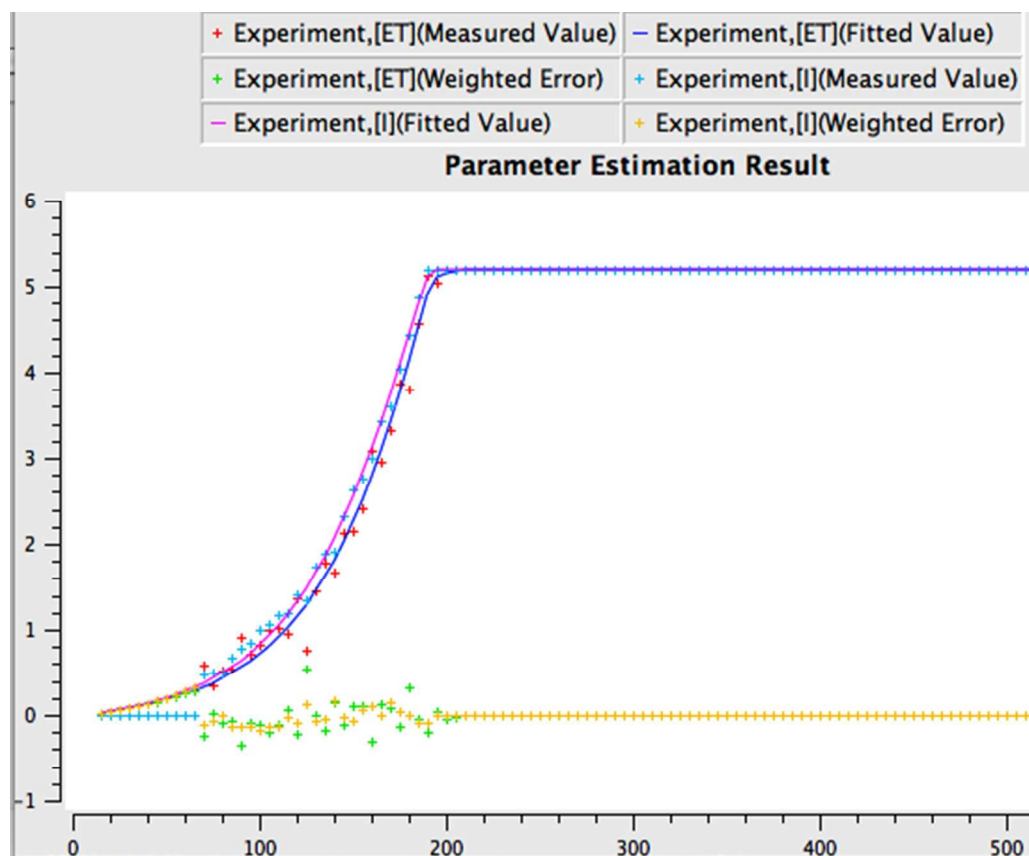


Figure S5. Acidic water model fit of phases 1 and 2.

Table S2. Acidic water model equations.

# ▲	Name	Equation
1	R1	$AA + C = A + CA$
2	R2	$A \rightarrow V$
3	R3	$V + AA \rightarrow W + I + ET$
4	R4	$ET + W = EH + C$
5	R5	$CA = A + C$

Table S3. Acidic water model initial concentrations.

Initial Concentrations

A	indep	0	mmol/ml
AA	indep	9	mmol/ml
C	indep	0.0298423	mmol/ml
CA	dep	0	mmol/ml
EH	dep	0	mmol/ml
ET	indep	0	mmol/ml
I	dep	0	mmol/ml
V	indep	0	mmol/ml
W	dep	0	mmol/ml

Table S4. Acidic water model fitted parameters.

	Parameter	Value	Std. Deviation	Coeff. of Variation [%]	Gradient
1	[C]_0	0.0298423	0.00387925	12.9992	8.05699
2	(R1).k1	58.3114	98.607	169.104	0.00136543
3	(R1).k2	9.19174e-09	4.26857e-07	4643.92	277633
4	(R2).k1	0.0293634	0.00113495	3.86519	11.9949
5	(R3).k1	3.21848e+06	2.39385e+08	7437.83	6.15097e-10
6	(R4).k1	0.0780294	0.105282	134.926	0.957578
7	(R4).k2	7736.43	17166.7	221.895	9.05877e-06
8	(R5).k1	0.115835	0.00971665	8.38834	5.50601
9	(R5).k2	2.62463e-05	0.00196788	7497.74	74.7869

	Experiment	Objective Value	Root Mean Square	Error Mean	Error Mean Std. Deviation
1	Experiment	1.87042	0.0905738	0.00654225	0.0903372

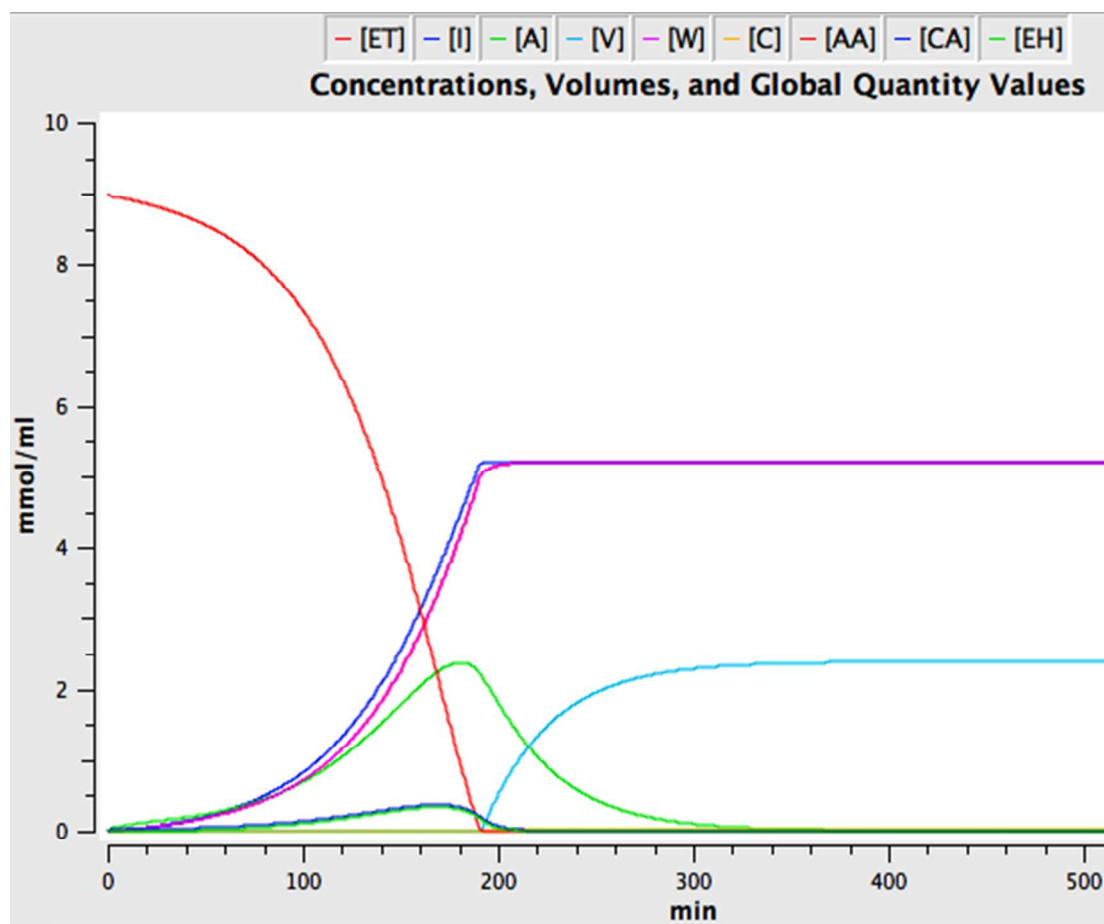


Figure S6. Phases 1 and 2 acidic water model simulation using fitted parameters.

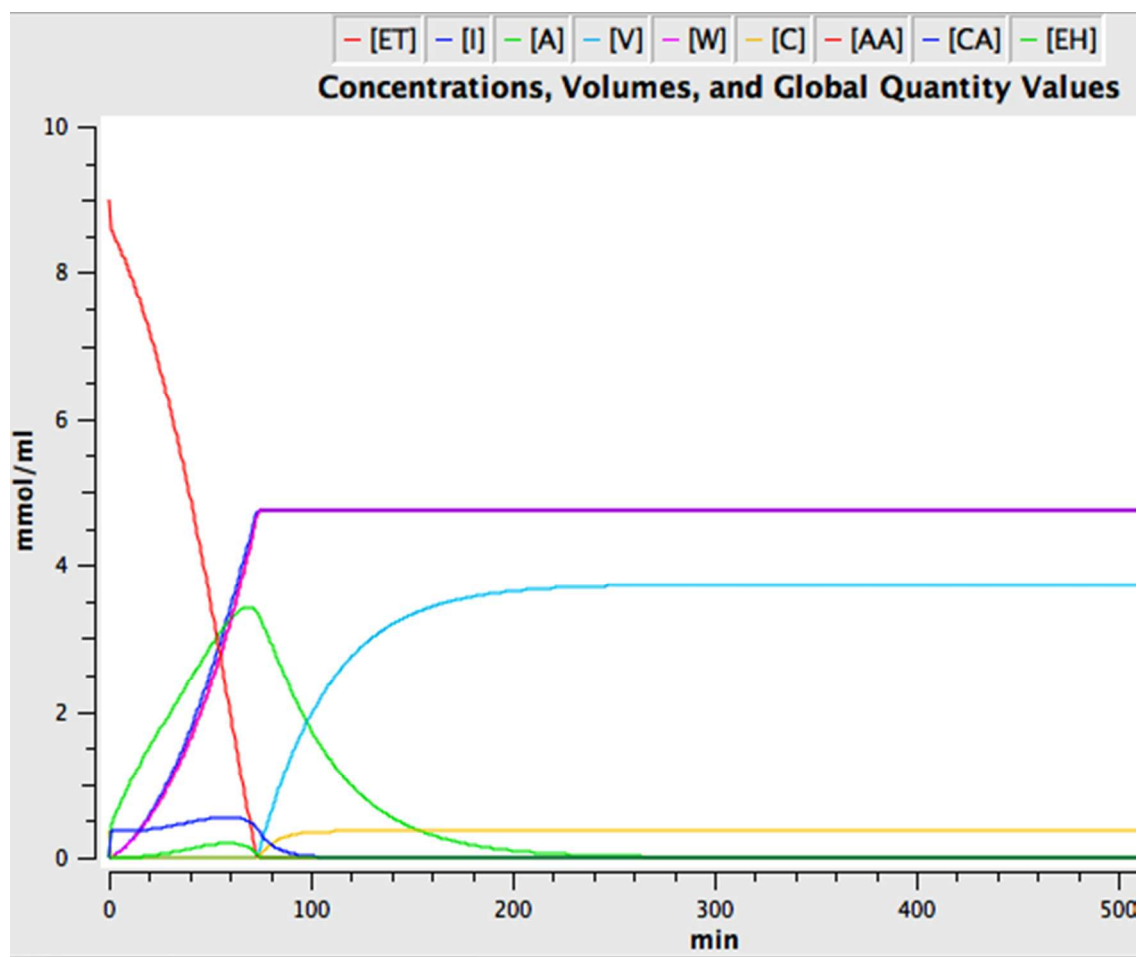


Figure S7. Phases 1 and 2 acidic water model simulation with 4% H^+

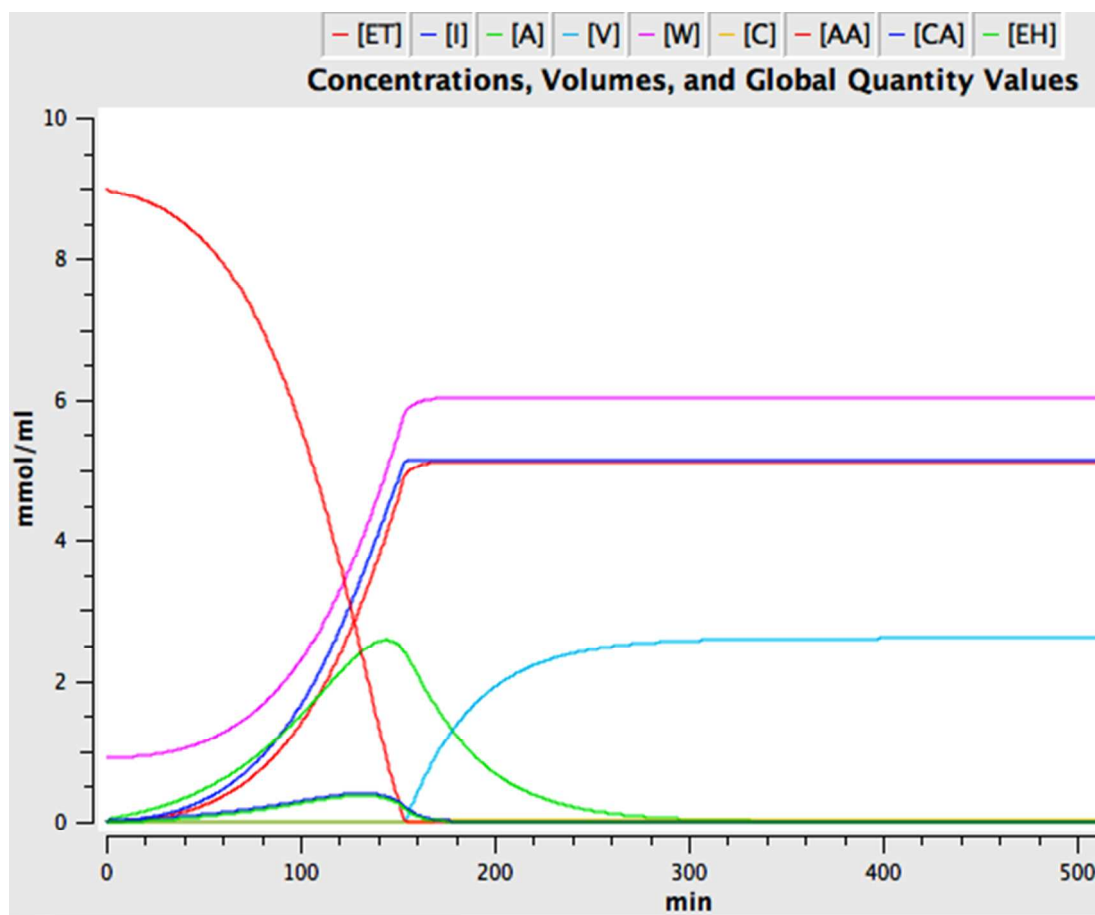


Figure S8. Phases 1 and 2 acidic water model simulation with 10% initial water.

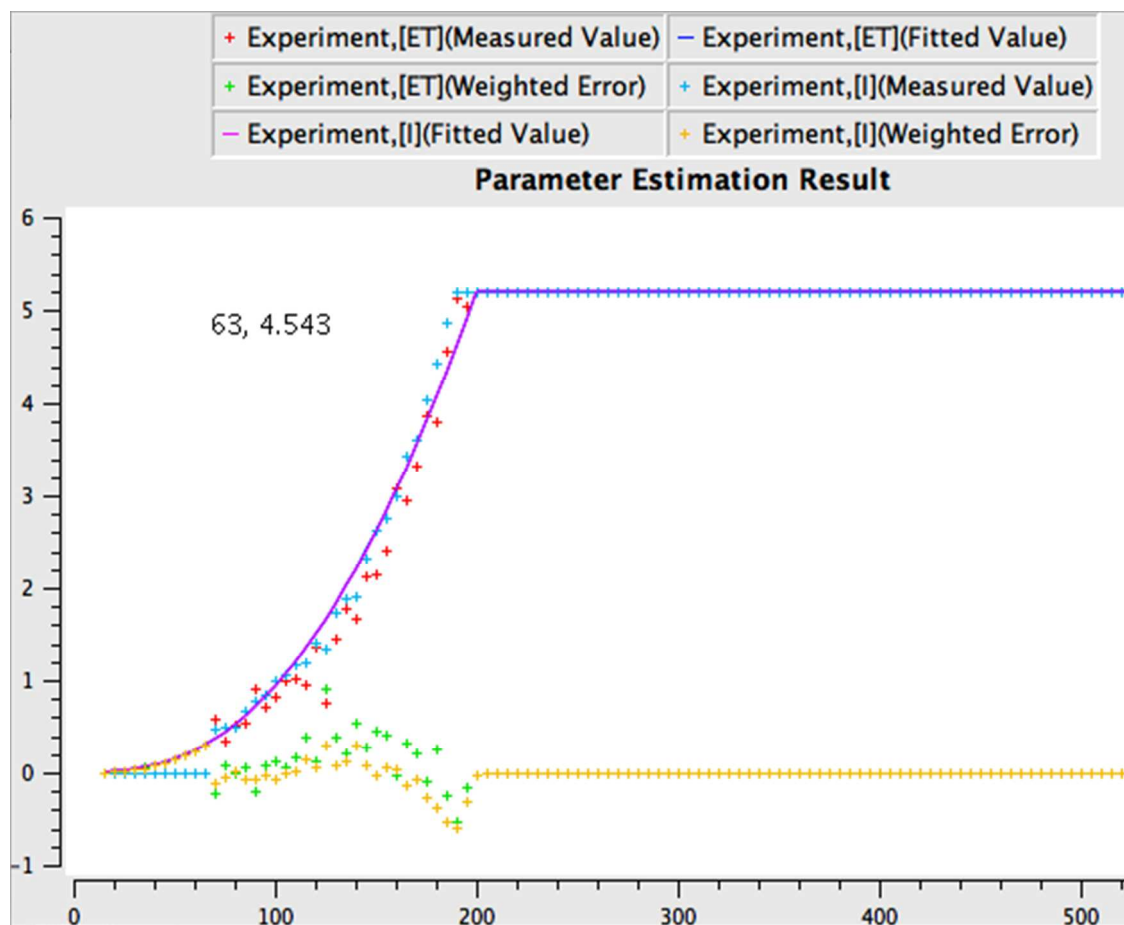
B) $\text{Pt}(\text{COD})(\text{OTf})_2$ (BT) impurity (1%) model with fitted parameters

Table S5. Impurity model equations.

# ▲	Name	Equation
1	R1	$\text{BT} \rightarrow \text{C} + \text{ET}$
2	R2	$\text{AA} + \text{C} \rightarrow \text{A} + \text{CA}$
3	R3	$\text{A} \rightarrow \text{V}$
4	R4	$\text{V} + \text{AA} \rightarrow \text{W} + \text{I} + \text{ET}$
5	R5	$\text{CA} = \text{C} + \text{A}$

Table S6. Impurity model initial concentrations.

Initial Concentrations				
A	indep	0	mmol/ml	
AA	dep	9	mmol/ml	
BT	dep	0.09	mmol/ml	
C	indep	0	mmol/ml	
CA	indep	0	mmol/ml	
ET	indep	0	mmol/ml	
I	dep	0	mmol/ml	
V	indep	0	mmol/ml	
W	dep	0	mmol/ml	

**Figure S9.** Impurity model fit of phases 1 and 2 (1% BT).**Table S7.** Impurity model fitted parameters.

	Parameter	Value	Std. Deviation	Coeff. of Variation [%]	Gradient
1	(R1).k1	1.28502e-05	0.000399817	3111.37	30474.5
2	(R2).k1	1355.95	41706.9	3075.84	-8.75147e-06
3	(R3).k1	0.0229481	0.0032591	14.202	6.64666
4	(R4).k1	1.7758e+09	1.92549e+11	10842.9	1.37983e-12
5	(R5).k1	175.514	5459.97	3110.85	0.00214044

	Experiment	Objective Value	Root Mean Square	Error Mean	Error Mean Std. Deviation
1	Experiment	4.36164	0.138311	0.0153077	0.137462

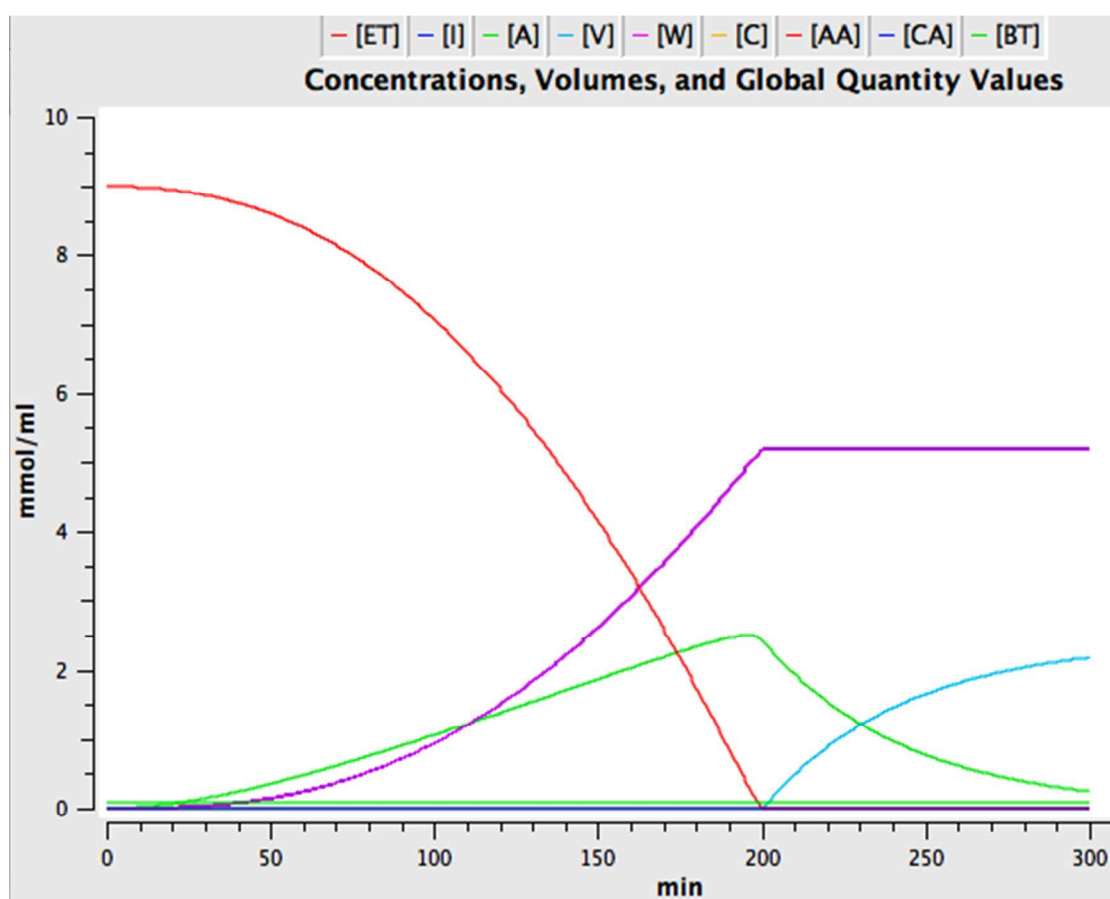


Figure S10. Phases 1 and 2 impurity model simulation using fitted parameters (1% BT).

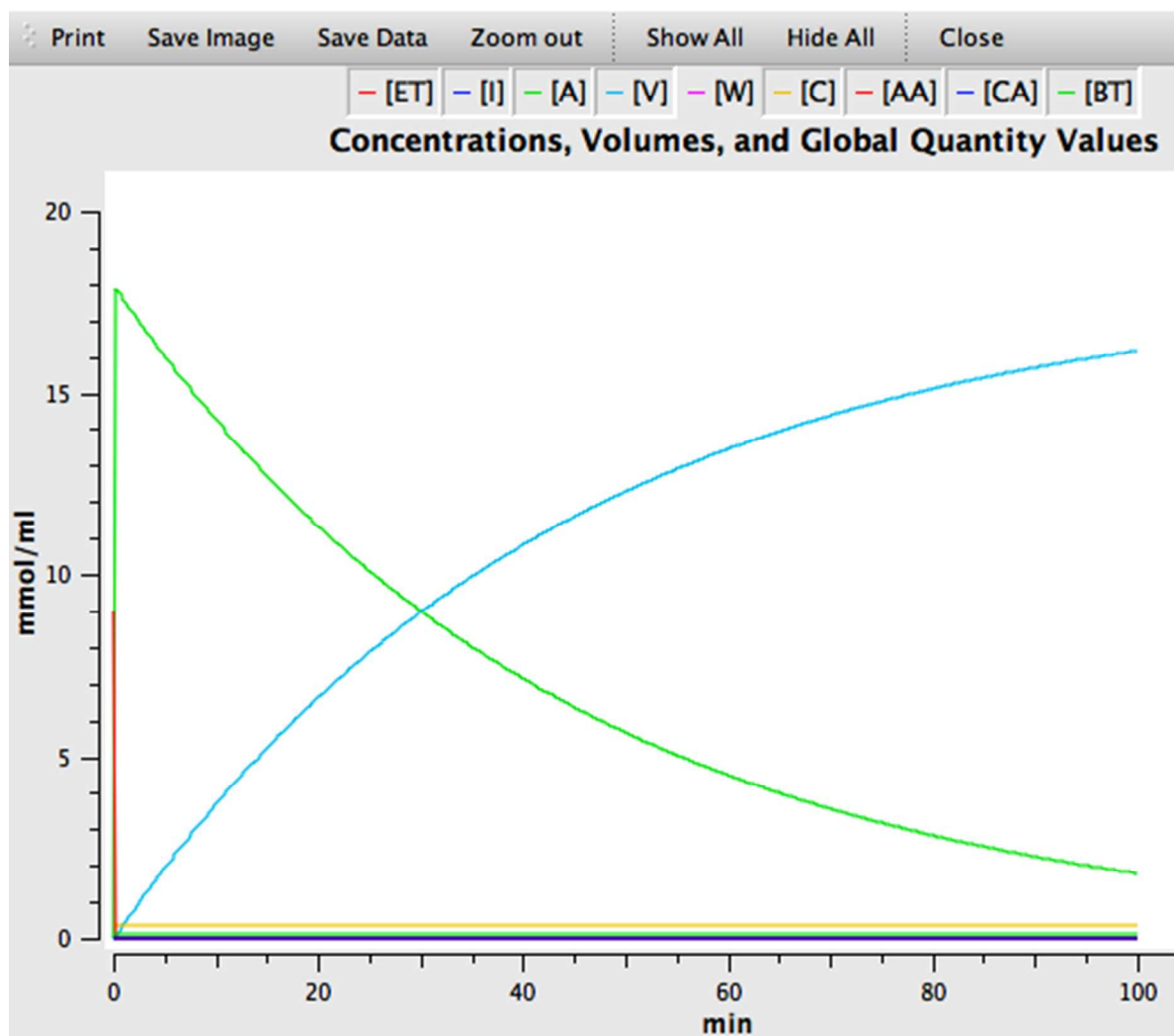


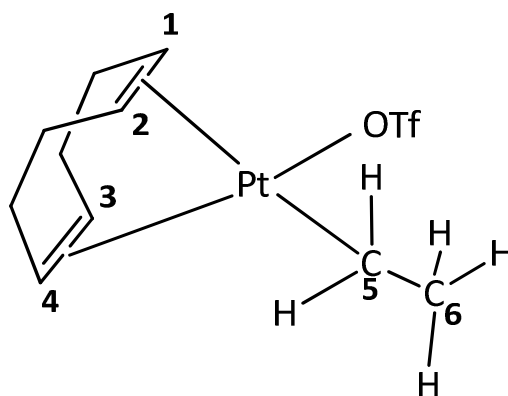
Figure S11. Phases 1 and 2 impurity model simulation with 4% H^+ (1% BT). Upper green line is monomer A. Dimer AA (**4**) is consumed in less than 1 min.

Experimental

General Procedures. All experiments were conducted under a dinitrogen atmosphere in a Vacuum Atmosphere Corporation drybox unless otherwise noted. Solvents were dried under standard techniques and were stored in the drybox, over 4Å molecular sieves or sodium metal. Chemicals were purchased from the following companies: Ethylene from Scott Specialty Gases, propylene from Linweld Lincoln, CD_3NO_2 from Acros, and HOTf and polymerbound base- NEt_2 (100-200 mesh, 1% cross linked, typical loading 1.0-1.5 mmol/g) were purchased from Aldrich. CD_2Cl_2 was purchased from Cambridge Isotope Laboratories. All commercial chemicals were used as received. Corannulene,² $[\text{Pt}(\text{COD})(\text{OH})_2][\text{OTf}]_2$ (**4**),³ $\text{Pt}(\text{COD})\text{Et}_2$,⁴ and

$\text{Pt}(\text{COD})(\text{OTf})_2^5$ were synthesized according to literature procedures. NMR spectra were recorded on Bruker AMX -300 or -500 spectrometers at ambient temperatures except where noted. All NMR chemical shifts (δ) are reported in ppm with coupling constants in Hz. ^1H NMR chemical shifts are relative to protio solvent signals referenced to TMS (0 ppm), ^{13}C NMR chemical shifts are relative to internal solvent signals referenced to TMS (0 ppm) and ^{195}Pt NMR chemical shifts are relative to external $\text{K}_2\text{PtCl}_4/\text{D}_2\text{O}$ (-1,624 ppm).

Acetaldehyde yield determination. In the following reactions the amount of acetaldehyde was determined by integration of the aldehydic proton signal at δ 9.75. In many cases the yield thus obtained appeared to be unreasonably low and we suspected signal saturation from a long relaxation time for the aldehydic proton. This was confirmed for an O_2 -free sample of acetaldehyde in CDCl_3 . The T1 of the aldehydic proton was found to be 23 s. To overcome the integration error caused by this long relation time we determined a correction factor by integrating both the methyl group and the aldehydic proton of acetaldehyde under conditions similar to those used in the experiments below. Assigning an integration value of 3 to the methyl group gave an integration value of 0.7 for the aldehydic proton. Therefore, all of the aldehydic proton integration values for the experiments below have been divided by 0.7.



Atom labeling for the NMR data of $(\text{COD})\text{Pt}(\text{Et})(\text{OTf})$ (**6**)

$\text{Pt}(\text{COD})(\text{Et})(\text{OTf})$ (6**).** Inside the drybox, HOTf (20.7 μL , 0.234 mmol) was added to a yellow solution of $\text{Pt}(\text{COD})(\text{Et})_2$ (85.0 mg, 0.235 mmol) in 0.45 mL CD_2Cl_2 in a screw cap NMR tube. The contents were mixed and immediately the solution turned dark red and $\text{Pt}(\text{COD})(\text{Et})(\text{OTf})$ (**6**) was formed in over 90% yield, accompanied by evolution of ethane. Also signals for trace amounts of $(\text{COD})\text{Pt}(\text{OTf})_2$ and a Pt-hydride complex (see text) were found. Complex **6** was characterized by ^1H , ^{13}C , DEPT, ^1H - ^{13}C HMQC and ^{195}Pt NMR spectroscopy. Upon standing in solution **6** decomposes to give $\text{Pt}(\text{COD})(\text{OTf})_2$ and ethane.

^1H NMR (500 MHz, CD_2Cl_2): 5.81 (m with Pt satellites, $J_{\text{Pt-H}} = 24.5$ Hz, 2H, COD CH's 1 & 2) 4.41 (m with Pt satellites, $J_{\text{Pt-H}} = 97.5$ Hz, 2H, COD CH's 3 & 4), 2.6 - 2.2 (m, 8H, COD CH_2), 1.54 (q with Pt satellites, $J_{\text{H5-H6}} = 7.5$ Hz, $J_{\text{Pt-H}} = 70.0$ Hz, 2H, CH_3CH_2 at 5), 0.89 (t, $J_{\text{H5-H6}} = 7.5$ Hz, 3H, CH_3CH_2 at 6), ^{13}C NMR (126 MHz, CD_2Cl_2) 116.9 (s with Pt

satellites, $J_{\text{Pt-C}} = 21.1$, COD 1 & 2), 79.7 (s with Pt satellites, $J_{\text{Pt-C}} = 294.3$, COD 3 & 4), 31.3, 27.2 (COD methylenes), 21.4 (s with Pt satellites, $J_{\text{Pt-C}} = 584.5$, CH_3CH_2 at 5), 14.2 (s, CH_3CH_2 at 6), ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3469 (s). Observation of ethane, ^1H NMR (500 MHz, CD_2Cl_2): 0.84 (s). Signal for Pt-H: ^1H NMR (500 MHz, CD_2Cl_2): -1.96 (s, with Pt satellites $J_{\text{Pt-H}} = 775.5$ Hz). Characteristic signals for $(\text{COD})\text{Pt}(\text{OTf})_2$: ^1H NMR (500 MHz, CD_2Cl_2): 6.27 (s with Pt satellites $J_{\text{Pt-H}} = 78.4$ Hz) and ^{195}Pt NMR (64 MHz, CD_2Cl_2): -2990 (s).

Pt(COD)(Et)(OTf) (6) with added C_2H_4 : $[\text{Pt}(\text{COD})(\text{Et})(\text{C}_2\text{H}_4)](\text{OTf})$ (7). Similar to the above procedure a sample of **6** was prepared in a screw cap NMR tube from a reaction between HOTf (6.0 μL , 0.069 mmol) and $(\text{COD})\text{Pt}(\text{Et})_2$ (25.0 mg, 0.069 mmol) in 0.55 mL CD_2Cl_2 . Ethylene (3.2 mL) was injected via the screw cap septum and the contents thoroughly mixed. The solution remained dark red. In this case complex **6** remains stable for days. $[\text{Pt}(\text{COD})(\text{Et})(\text{C}_2\text{H}_4)](\text{OTf})$ (**7**) is present as evident from the upfield peaks in the ^1H NMR (300 MHz) at 0.41 (q, $J_{\text{H-H}} = 7.5$, $J_{\text{Pt-H}} = 84.5$, CH_3CH_2) and -0.33 (t, $J_{\text{H-H}} = 7.5$, $J_{\text{Pt-H}} = 42.5$, CH_3CH_2) and ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3874. At -20°C, ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3483 (s). At -50°C, ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3493 (s). The mixture was also studied by EXSY in a 300-AMX probe at ambient temperature (see text).

Complexes 6 and 7 with added H_2O . The above NMR tube with contents was opened outside the drybox and immediately de-ionized H_2O (15.0 μL , 0.083 mmol) was added. The screw cap was closed and ethylene (2.0 mL) was injected via the screw cap septum. The contents were thoroughly mixed by shaking. The resulting mixture was characterized by ^1H , ^{13}C , DEPT, ^1H - ^{13}C , HMQC, EXSY and ^{195}Pt NMR spectroscopy. ^1H NMR analysis showed signals for **6** and **7** and the following additional signals. ^1H NMR (300 MHz, CD_2Cl_2): 3.45 (s, br), 3.17 (s with Pt satellites $J_{\text{Pt-H}} = 56.7$ Hz). ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3543 (s), -3872 (s, trace), -3990 (s, br). At -20°C: ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3555 (s), -3913 (s, trace), -4039 (s, trace). At -50°C: ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3560 (s), -3928 (s, trace), -4057 (s, trace)

Ethylene reaction profiles for $[\text{Pt}(\text{COD})(\text{OH})]_2(\text{OTf})_2$ (4**) in CD_2Cl_2 .** The following experiments were performed using the same batch of **4** and of the same CD_2Cl_2 . Corannulene was added as an integration standard. **(A) Control:** Outside the drybox, corannulene (0.9 mg, 0.004 mmol) was measured into a screw cap NMR tube. The tube was taken into the drybox and **4** (5.0 mg, 0.0053 mmol) was added. The solids were dissolved in 0.65 mL CD_2Cl_2 and the tube was sealed, removed from the drybox and placed in a dry ice/acetone bath. Ethylene (3.6 mL, 0.15 mmol) was injected via the screw cap septum. The NMR tube was taken out of the bath, the contents were mixed well by shaking and the tube was immediately placed in the NMR probe (AMX-300 MHz) at ambient temperature. The ensuing reaction was monitored by ^1H NMR spectroscopy. **(B) 10 % H_2O :** A solution of **4** (5.0 mg, 0.0053 mmol) and corannulene (1.3 mg, 0.0052 mmol) in 0.65 mL CD_2Cl_2 was prepared similar to the above procedure. The NMR tube was taken out from the drybox and H_2O (2.0 μL of a freshly prepared

solution of 20 μL of H_2O in 4000 μL of CDCl_3) was added through the screw cap septum. The tube was then placed in a dry ice/acetone bath. Ethylene addition and reaction monitoring were similar to that described in A. **(C) 4% HOTf:** A solution of **4** (5.0 mg, 0.0053 mmol) and corannulene (1.5 mg, 0.0059 mmol) in 0.65 mL CD_2Cl_2 was prepared similarly to the above procedure. HOTf (2.0 μL of a freshly prepared 0.011 M stock solution of HOTf in CDCl_3) was added. The tube was then placed in a dry ice/acetone bath. Ethylene addition and reaction monitoring were similar to that described in A. **(D) 10% (COD)Pt(OTf)₂:** A solution of **4** (5.0 mg, 0.0053 mmol) and corannulene (0.9 mg, 0.004 mmol) in 0.65 mL CD_2Cl_2 was prepared similar to the above procedure. (COD)Pt(OTf)₂ (32.0 μL of a freshly prepared 0.017 M stock solution in CDCl_3) was added at 25°C. Ethylene addition and reaction monitoring were similar to that described in A. **(E) Low ethylene concentration:** A solution of **4** (5.0 mg, 0.0053 mmol) and corannulene (0.8 mg, 0.0032 mmol) in 0.65 mL CD_2Cl_2 was prepared in a screw cap NMR tube. The tube was placed in a dry ice/acetone bath and ethylene (1.0 mL, 0.041 mmol) was injected via the screw cap septum. The NMR tube was taken out from the cold bath, the contents were mixed well by shaking and the tube was immediately placed in the NMR probe (AMX-300MHz) at ambient temperature. The ensuing reaction was monitored by ^1H NMR spectroscopy.

Ethylene reaction profile for [Pt(COD)(OH)]₂(OTf)₂ (4**) in CD_3NO_2 :** Following a procedure similar to that for CD_2Cl_2 above, a ^1H NMR reaction profile was obtained in CD_3NO_2 (0.50 mL) with corannulene (1.1 mg, 0.0044 mmol), **4** (5.0 mg, 0.0053 mmol) and ethylene (4.0 mL). After 48 h, the volatiles were removed and the resulting yellow residue was dissolved in acetone- d_6 and the residue characterized by ^1H and ^{195}Pt NMR spectroscopy at -60°C. Allyl complex [Pt(COD)(η^3 -CH₂CHCHCH₃)]OTf was detected as the only Pt containing product.

Ethylene reaction of [Pt(COD)(OH)]₂(OTf)₂ (4**): Variable temperature ^1H and ^{195}Pt NMR spectroscopy.** Similar to the above procedure a CD_2Cl_2 solution of **4** (5.0 mg, 0.0053 mmol) and corannulene (1.2 mg, 0.0048 mmol) was prepared in a screw cap NMR tube and ethylene (4.0 mL) was injected via the screw cap septum at RT. The contents were mixed well by shaking and the tube was placed in the NMR probe (AMX-300 MHz). After ~1 h the reaction was examined at ambient temperature, 0 °C and -50 °C. The probe and sample were warmed to 27 °C to allow the reaction to continue. After ~25 min ^1H NMR spectroscopy showed that **4** had been consumed to produce Pt(COD)(Et)(OTf) (**6**), [Pt(COD)(Et)(C₂H₄)]OTf (**7**) (Yield of **6** plus **7** = 50%), [Pt₂(COD)₂(μ -OH){ μ - κ^2 -C,O-CH₂C(O)H}](OTf)₂ (**10**) and (COD)Pt(CH₂C(O)H)(OTf) (**11**). At this point the probe and sample were cooled and the sample was analyzed at -20 °C and -50 °C. The probe and sample were then warmed to 27 °C to allow the reaction to continue. After ~1 h, ^1H NMR analysis at 27 °C showed ~ 70% yield of **6** plus **7**. The probe and sample were cooled and the sample was again analyzed at -20°C and -50°C.

Ethylene reaction of [Pt(COD)(OH)]₂(OTf)₂ (4**): Exchange Spectroscopy (EXSY).** Inside the dry box, a solution of **4** (12.0 mg, 0.0128 mmol) in 0.5 mL CD_2Cl_2 was prepared in a screw cap NMR tube. The tube was removed from the dry box and ethylene (2.20 mL) was injected via the screw cap septum. Approximately 1.5 h later, all

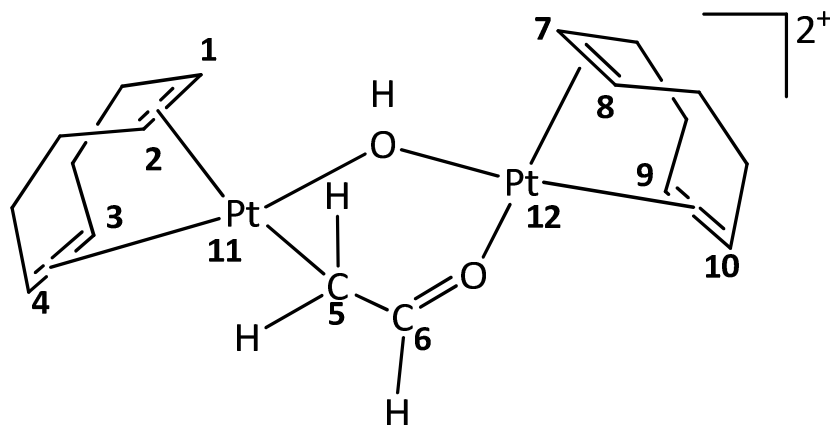
4 was consumed to produce (COD)Pt(Et)(OTf) (**6**), [(COD)Pt(Et)(C₂H₄)]OTf (**7**), [Pt₂(COD)₂(μ-OH){μ-κ²-C,O-CH₂C(O)H}](OTf)₂ (**10**) and (COD)Pt(CH₂C(O)H)(OTf) (**11**) as evidenced by ¹H NMR spectroscopy. The sample was then examined by EXSY in the 500-AMX NMR probe.

Ethylene reaction of [Pt(COD)(OH)]₂(OTf)₂ (4**): Effect of HOTf on the yield of acetaldehyde.** The following reactions were performed using the same batch of **4** and the same CD₂Cl₂. Acetaldehyde yields are reported with respect to the sum of (COD)Pt(Et)(OTf) (**6**) and [(COD)Pt(Et)(C₂H₄)]OTf (**7**) (assumed 100% yield). **(A) 1 equiv of HOTf:** Inside the dry box, a solution of **4** (6.0 mg, 0.0064 mmol) in 0.62 mL CD₂Cl₂ was prepared in a screw cap NMR tube and neat HOTf (0.6 μL, 0.007 mmol) was added. ¹H NMR spectroscopy (AMX-300) showed broad peaks at δ 9.4 and δ 6.9 and the formation of Pt(COD)(OTf)₂ (δ 6.26 s, J_{Pt-H} = 80.1 Hz, COD CH's and 2.87-2.26 COD CH₂'s). ¹⁹⁵Pt NMR spectroscopy (64 MHz) confirmed the presence of Pt(COD)(OTf)₂ (δ -2989). The tube was taken out of the drybox, and ethylene (3.0 mL) was injected through the screw cap septum. The contents were well mixed by shaking and allowed to react for 24 hr at 25°C (acetaldehyde yield = 17%). **(B) 20% HOTf:** Similarly a solution of **4** (6.0 mg, 0.0064 mmol) in 0.70 mL CD₂Cl₂ was prepared in a screw cap NMR tube and HOTf (2.2 μL of a freshly prepared 0.59 M stock solution in CDCl₃) was introduced. ¹H NMR spectroscopy showed that the peaks for **4** had broadened. The tube was placed in a dry ice/acetone bath and ethylene (3.0 mL, 0.12 mmol) was injected via the screw cap septum. Similar to the above procedure, the contents were mixed and the reaction was monitored by ¹H NMR spectroscopy at ambient temperature (acetaldehyde yield = 43 %). **(C) 10% HOTf:** As before a solution of **4** (6.0 mg, 0.0064 mmol) in 0.70 mL CD₂Cl₂ was prepared in a screw cap NMR tube and HOTf (1.1 μL of a freshly prepared 0.59 M stock solution in CDCl₃) was introduced. The tube was placed in a dry ice/acetone bath and ethylene (3.0 mL) was injected via the screw cap septum. The contents were mixed by shaking and immediately placed in the NMR probe (AMX-300MHz) at ambient temperature. The reaction was monitored by ¹H NMR spectroscopy and was completed within an hour (acetaldehyde yield = 71%).

Ethylene reaction of [Pt(COD)(OH)]₂(OTf)₂ (4**): Effect of ~NEt₂.** The effect of the base was tested by adding it at different stages of the reaction. **(A) Initial:** Inside the drybox, ~ 2 mg of polymer-bound base-NEt₂ was added to a pale yellow solution of **4** (6.0 mg, 0.0064 mmol) in 0.60 mL CD₂Cl₂ in a screw cap NMR tube. The contents were mixed by shaking and immediately the solution became deep yellow. Ethylene (3.0 mL) was added at RT by injecting through the screw cap septum. The contents were mixed by shaking and the reaction was monitored by ¹H NMR spectroscopy (300-AMX). Signals for **4** were broadened and after 24 h, a complicated NMR spectrum of unknown compounds resulted. No acetaldehyde was detected. **(B) Halfway through reaction:** Inside the drybox a solution of **4** (4.5 mg, 0.0048 mmol) in 0.45 mL CD₂Cl₂ was prepared in a screw cap NMR tube and ethylene (1.0 mL) was added via the screw cap septum. Once the reaction had proceeded to make **10** and trace amount of **11** and acetaldehyde (by ¹H NMR spectroscopy) the tube was taken into the drybox. The screw cap top was opened and ~ 2-3 mg of ~NEt₂ was quickly added. The tube was resealed and the mixture was shaken and removed from the drybox. ¹H NMR spectroscopy

confirmed that no significant amount of ethylene had escaped. The reaction was studied by ^1H and ^{195}Pt NMR spectroscopy. ^1H NMR signals for **4** were broadened and after 12 h, spectra showed new peaks of unknown origin. No further acetaldehyde formed. Signals for unknown compound(s): ^1H NMR (300 MHz, CD_2Cl_2): 9.17 (d, $J_{\text{H-H}} = 9.60$ Hz), 8.65 (s), 4.78 (br, m), 3.96 (m), ^{195}Pt NMR (CD_2Cl_2 , 64 MHz) : -3310, -3079. **(C) End of reaction:** A solution of **4** (5 mg, 0.0053 mmol) in CD_2Cl_2 (0.65 mL) was prepared inside the drybox. Outside the drybox ethylene (3.6 mL) was added at RT via the screw cap septum. After 12 hr, the reaction was completed to produce acetaldehyde and the Pt-ethyl complexes, **6** and **7**. The tube was taken into the drybox, the screw cap opened and ~3 mg of $\sim\text{NEt}_2$ was quickly added followed by immediate recapping of the NMR tube. The contents were mixed well by shaking. The reaction was studied by ^1H NMR spectroscopy. Observed additional signals: ^1H NMR (500 MHz, CD_2Cl_2): 7.06 (s, br), 6.61 (s, br), 3.18 (s with Pt satellites, $J_{\text{Pt-H}} = 56.7$ Hz), 1.86 (s, br), -1.96 (with Pt satellites, $J_{\text{Pt-H}} = 776$ Hz).

Vinyloxy-trimethylsilane ($\text{CH}_2\text{CHOSiMe}_3$) reaction of **4:** $[\text{Pt}_2(\text{COD})_2(\mu\text{-OH})\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C(O)H}\}](\text{OTf})_2$ (**10**) and $(\text{COD})\text{Pt}(\text{CH}_2\text{C(O)H})(\text{OTf})$ (**11**). **(A) In CDCl_3 :** CDCl_3 (0.60 mL passed through activated Al_2O_3), was transferred to an NMR tube and $\text{CH}_2\text{CHOSiMe}_3$ (2.4 μL , 0.016 mmol) was added. Solid **4** (5.0 mg, 0.053 mmol) was then added and the tube was shaken to mix the contents. **(B) In CD_2Cl_2 :** Following a procedure similar to the above, a mixture of **10** and **11** was prepared in CD_2Cl_2 by reacting $\text{CH}_2\text{CHOSiMe}_3$ (2.3 μL , 0.015 mmol) with **4** (5.0 mg, 0.053 mmol) in CD_2Cl_2 (0.55 mL). Both complexes were characterized by ^1H , ^1H - ^1H COSY, ^{13}C , ^{13}C -DEPT, ^1H - ^{13}C HMQC, ^{195}Pt and ^1H - ^{195}Pt HMQC and EXSY NMR spectroscopy. ^1H - ^{195}Pt HMQC spectroscopy was done in a 300-AMX probe and EXSY was done in a 500-AMX probe (mixing time = 800 ms) at ambient temperature. A solution of **11** free of **10** was prepared by increasing the amount of $\text{CH}_2\text{CHOSiMe}_3$ to 4.3 μL (0.028 mmol) using the same amount of **4**.



Atom labeling scheme for $[\text{Pt}_2(\text{COD})_2(\mu\text{-OH})\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C(O)H}\}](\text{OTf})_2$ (**10**)

Data for **10** in CDCl₃:

H or C assignment	¹ H NMR (300 MHz, CDCl ₃)	¹³ C NMR (125 MHz, CDCl ₃)
OH	7.46 (s)	-
1,2	6.11 (m with Pt satellites, J _{Pt-H} = 34.5 Hz)	114.2
3,4	5.25 (m with Pt satellites, J _{Pt-H} = 68.0 Hz)	88.5
5	3.99 (d with satellites, J _{H5-H6} = 6.0 Hz, J _{Pt-H} = 74.0 Hz)	47.9
6	9.25 (t with broad unresolved satellites, J _{H5-H6} = 6.0 Hz)	208.9
7,8 & 9,10	6.26 (br, s) & 5.67 (br s)	102.8 & 98.6
COD CH ₂ 's	2.70- 2.28 (m, COD CH ₂ 's)	

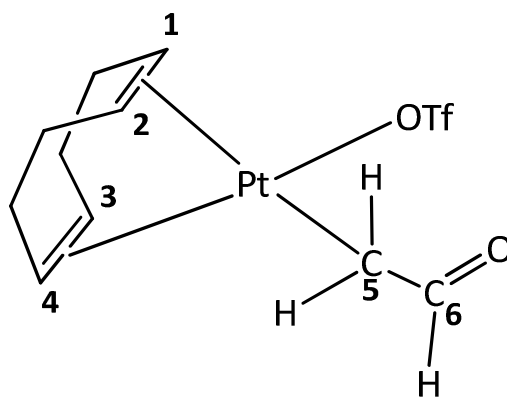
¹⁹⁵Pt NMR (64 MHz, CDCl₃) -3065 (s, Pt 12), -3410 (s, Pt 11) equal intensities.

Data for **10** in CD₂Cl₂: ¹H NMR (300 MHz, CD₂Cl₂): 9.31 (t with broad unresolved satellites, J_{H5-H6} = 6.3 Hz, 1H, H6,), 7.52 (s, 1H, bridging OH) 6.24 (br s with Pt satellites, J_{Pt-H} = 69.0 Hz, 2H, COD CH's at 7, 8 or 9,10), 6.11 (m with satellites, J_{Pt-H} = 23.4 Hz, 2H, COD CH's at 1,2), 5.67 (br s, 2H, COD CH's at 7,8 or 9,10), ~ 5.30 (m overlapping with solvent signal at 5.32 ppm, 2H, CH's at 3,4), 3.94 (d with satellites, J_{H5-H6} = 6.3 Hz, J_{Pt-H} = 80.1 Hz, 2H, H5), 2.70- 2.25 (m, COD CH₂'s)

¹⁹⁵Pt NMR (64 MHz, CD₂Cl₂): -3080 (s), -3417 (s) (1:1 ratio).

¹⁹⁵Pt NMR (64 MHz, CD₂Cl₂) at -20°C: -3101 (s), -3434 (s) (1:1 ratio).

¹⁹⁵Pt NMR (64 MHz, CD₂Cl₂) at -50°C: -3110 (s), -3442 (s) (1:1 ratio).



Atom labeling for the NMR data of Pt(COD)(CH₂C(O)H)(OTf) (**11**)

Data for **11** in CDCl₃: ¹H NMR (500 MHz, CDCl₃): 9.67 (t, J_{H5-H6} = 4.5 Hz 1H, H6,), 5.95 (m with Pt satellites, J_{Pt-H} = 30.5 Hz, 2H, COD CH's at 1,2), 4.85 (m, J_{Pt-H} = 86.5 Hz, 2H, COD CH's 3,4), 2.84 (d with Pt satellites, J_{H5-H6} = 4.5 Hz, J_{Pt-H} = 81.5 Hz, 2H, H5), 2.70- 2.28 (m, COD CH₂'s), ¹³C NMR (126 MHz, CDCl₃): 115.5 (s, C1,2), 86.2 (s, C3,4),

37.8 (s, C5), A signal for C6 is not observed (see text). ^{195}Pt NMR (64 MHz, CDCl_3) - 3342 (s).

Data for **11** in CD_2Cl_2 : ^1H NMR (300 MHz, CD_2Cl_2): 9.65 (t, $J_{\text{H5-H6}} = 4.5$ Hz, 1H, H6), 5.91 (m with Pt satellites, $J_{\text{Pt-H}} = 50.1$ Hz, 2H, COD CH's at 1 & 2), 4.87 (m with Pt satellites, $J_{\text{Pt-H}} = 86.4$ Hz, 2H, COD CH's at 3 & 4), 2.83 (d with Pt satellites, $J_{\text{H5-H6}} = 4.5$ Hz, $J_{\text{Pt-H}} = 84.0$ Hz, 2H, H5), 2.70- 2.25 (m, COD CH_2 's). ^{195}Pt NMR (64 MHz, CD_2Cl_2): - 3342 (s). At -20°C , ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3325 (s). At -50°C , ^{195}Pt NMR (64 MHz, CD_2Cl_2): -3311 (s).

Effect of HOTf on 10 & 11: Outside the drybox corannulene (1.3 mg, 0.0052 mmol) was measured into a NMR tube. The tube taken inside the drybox and dissolved in CDCl_3 (0.75 mL passed through activated Al_2O_3) and a couple of molecular sieves were added to quench any residual water in the solvent. $\text{CH}_2\text{CHOSiMe}_3$ (2.0 μL , 0.013 mmol) was added followed by **4** (5.0 mg, 0.0053 mmol). The contents were mixed by shaking and immediately analyzed by ^1H NMR spectroscopy in a 300-AMX probe which showed a 66:33 mixture of **10** and **11**. The NMR tube was taken into the drybox and aliquots of a freshly prepared 0.11 M stock solution of HOTf in CDCl_3 , were added consecutively; 1.0 μL , 2.0 μL , 3.0 μL , 4.0 μL and 5.5 μL . Between each addition, ~ 25 min were given for equilibration. After each addition the reaction was monitored by ^1H NMR and ^{195}Pt NMR spectroscopy in a 300-AMX probe.

^1H NMR: With each addition, signals belonging to **11** broadened and the intensity of **10** decreased.

^{195}Pt NMR (64 MHz, CDCl_3): Results shown in table below.

Effect of HOTf on **10** & **11**

Aliquots of 0.11 M HOTf	^{195}Pt NMR signals
No added HOTf	-3066, -3344, -3410
1.0 μL	-3066, -3410
3.0 μL	-2950, -3066, -3410

Ethylene reaction of 10 and 11. (A) CD_2Cl_2 (0.65 mL passed through activated Al_2O_3), was transferred to a screw cap NMR tube containing corannulene (0.8 mg, 0.003 mmol). $\text{CH}_2\text{CHOSiMe}_3$ (1.8 μL , 0.011 mmol) was added followed by solid **4** (5.0 mg, 0.00533 mmol) and the tube was placed in an ice/salt bath. Ethylene (3.6 mL, 0.14 mmol) was injected via the screw cap septum. The contents were mixed and immediately the NMR tube was placed in the NMR probe (AMX-300MHz) at ambient temperature. The reaction was monitored by ^1H NMR spectroscopy. **(B) With 1% HOTf:** A CD_2Cl_2 solution of **10**, **11** and corannulene was prepared as above. HOTf (1.0 μL from 0.055 M stock solution of HOTf in CDCl_3) was added and the tube was placed in an ice/salt bath. Ethylene (3.6 mL, 0.14 mmol) was injected via the screw cap septum and the reaction was monitored by ^1H NMR spectroscopy as above. **(C) With residual $[\text{Pt}(\text{COD})(\text{OH})_2(\text{OTf})_2]$ (**4**):** CD_2Cl_2 (0.65 mL passed through activated Al_2O_3), was transferred to a screw cap NMR tube containing corannulene (0.8 mg, 0.003 mmol). $\text{CH}_2\text{CHOSiMe}_3$ (1.8 μL , 0.011 mmol) was added followed by solid **4** (5.0 mg, 0.0053

mmol) and the tube was placed in a dry ice/acetone bath. Ethylene (3.8 mL, 0.15 mmol) was injected via the screw cap septum. The contents were mixed and the NMR tube was placed in the NMR probe (AMX-300MHz) at ambient temperature. The reaction was monitored by ^1H NMR spectroscopy.

HOTf reactions of $[\text{Pt}_2(\text{COD})_2(\mu\text{-OH})\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C(O)H}\}](\text{OTf})_2$ (10) and $(\text{COD})\text{Pt}(\text{CH}_2\text{C(O)H})(\text{OTf})$ (11). Separate reactions were carried out with additions of HOTf to a mixture (of **10** and **11**) and exclusively to **11**. **(A) Mixture of 10 and 11:** Outside the drybox, corannulene (1.3 mg, 0.0052 mmol) was measured into a NMR tube. The tube was taken into the drybox, and CDCl_3 (0.75mL passed through activated Al_2O_3), and $\text{CH}_2\text{CHOSiMe}_3$ (2.8 μL , 0.018 mmol) were transferred to it. Solid **4** (5.0 mg, 0.0053 mmol) was added and mixed well by shaking. ^1H and ^{195}Pt NMR showed a mixture of **10** and **11**. Neat HOTf (0.5 μL , 0.0053 mmol) was added and mixed well by shaking. The reaction mixture was immediately characterized by ^1H and ^{195}Pt NMR spectroscopy in a 300-AMX probe. ^1H NMR (300 MHz, CDCl_3): 6.24 (br), 5.97 (s with Pt satellites $J_{\text{Pt-H}} = 78.6$ Hz), 2.82 (br s), 2.02 (m). Acetaldehyde yield = 36%. ^{195}Pt NMR (64 MHz, CDCl_3): -2950 (major), -2985. **After 14 days:** ^1H NMR (300 MHz, CDCl_3): 5.75 (s, br), 5.27 (s), 2.77 (m, br), 2.6-2.4 (m,br) Acetaldehyde yield = 100%. ^{195}Pt NMR (64 MHz, CDCl_3): -2745. **(B) Only 11:** Outside the drybox, corannulene (1.2 mg, 0.0048 mmol) was measured into a screw cap NMR tube. The tube was taken into the drybox and CDCl_3 (0.75mL passed through activated Al_2O_3), and $\text{CH}_2\text{CHOSiMe}_3$ (5.0 μL , 0.033 mmol) were transferred to it. Solid **4** (5.5 mg, 0.0059 mmol) was added and mixed well by shaking. ^1H and ^{195}Pt NMR spectroscopy (300-AMX) showed a solution of exclusively **11**. HOTf (52.0 μL of 0.11 M solution in CDCl_3) was added and the contents mixed well by shaking. The reaction mixture was characterized by ^1H and ^{195}Pt NMR spectroscopy in a 300-AMX probe. ^1H NMR (300 MHz, CDCl_3): 6.28 (s with Pt satellites $J_{\text{Pt-H}} = 77.4$ Hz), 5.98 (s, br), 2.83 (s, br), 2.5 -2.2 (m, br). Acetaldehyde yield = 50%. At -20°C: ^1H NMR (300 MHz, CDCl_3): 6.26 (s with Pt satellites $J_{\text{Pt-H}} = 77.4$ Hz), 5.94 (s), 2.83 (m), 2.5 -2.2 (m, br). ^{195}Pt NMR (64 MHz, CDCl_3): -2950, -2985 (major). At -20°C: ^{195}Pt NMR (64 MHz, CDCl_3): -2969, -3000 (major).

The NMR tube with contents was taken back into the drybox and HOTf (52.0 μL of 0.11M solution in CDCl_3) was added and mixed well. The reaction mixture was studied by ^1H and ^{195}Pt NMR spectroscopy at ambient temperature.

^1H NMR (300 MHz, CDCl_3): 6.28 (s with Pt satellites $J_{\text{Pt-H}} = 77.4$ Hz), 6.10 (s, br), 2.83 (m), 2.03 (m overlapped with broad signals from 2.5-2.1). Acetaldehyde yield = 50%.

^{195}Pt NMR (300 MHz, CDCl_3): -2986

Ethylene (1.0 mL) was added by injecting through the screw cap septum and the sample was allowed to react for the next 12 hr.

^1H NMR (300 MHz, CDCl_3): 10.52 (s, br), and signals for **6**.

^{195}Pt NMR (64 MHz, CDCl_3): -3467.

In both reactions $(\text{COD})\text{Pt}(\text{OTf})_2$ is produced. Data for $(\text{COD})\text{Pt}(\text{OTf})_2$. ^1H NMR (300 MHz, CDCl_3): 6.29 (s with Pt satellites $J_{\text{Pt-H}} = 77.7$ Hz, 4H, COD CH's), 2.87 & 2.24 (m, 8H, COD CH_2 's). ^{195}Pt NMR (64 MHz, CDCl_3): -2990.

Water reaction of $[\text{Pt}_2(\text{COD})_2(\mu\text{-OH})\{\mu\text{-}\kappa^2\text{-C,O-CH}_2\text{C(O)H}\}](\text{OTf})_2$ (10**) and $(\text{COD})\text{Pt}(\text{CH}_2\text{C(O)H})(\text{OTf})$ (**11**).** Outside the drybox, corannulene (1.6 mg, 0.0064 mmol) was measured into an NMR tube. The tube was taken into the drybox, and CD_2Cl_2 (0.50 mL passed through activated Al_2O_3), and $\text{CH}_2\text{CHOSiMe}_3$ (6.5 μL , 0.043 mmol) were added. Solid **4** (10.0 mg, 0.011 mmol) was added and the contents mixed well by shaking. ^1H and ^{195}Pt NMR showed a 90:10 mixture of **10** and **11**. Outside the drybox, the NMR tube was opened and de-ionized H_2O (0.20 μL , 0.011 mmol) was added. The tube was closed and the contents mixed well by shaking. The reaction mixture was immediately characterized by ^1H and ^{195}Pt NMR spectroscopy. After 24 hr, characteristic ^1H and ^{195}Pt NMR signals of **4** were observed. ^1H NMR (300 MHz, CD_2Cl_2): 5.67 (s, br), 2.76 (m), 2.22 (m). ^{195}Pt NMR (64 MHz, CD_2Cl_2): -2762.

Ethylene reaction of $\text{Pt}(\text{COD})(\text{OTf})_2$. (A) In CD_3NO_2 : In the drybox, $\text{Pt}(\text{COD})(\text{OTf})_2$ (5.0 mg, 0.0083 mmol) was placed into a screw cap NMR tube and dissolved in 0.45 mL CD_3NO_2 . The NMR tube was placed in dry ice/acetone bath and ethylene (4.0 mL, 0.16 mmol) was injected via the screw cap septum. The tube was taken from the dry ice/acetone bath and contents mixed well by thoroughly shaking. The reaction was monitored by ^1H NMR spectroscopy in the 300-AMX probe and found to take ~ 2 h to reach completion to produce Pt-ethyl ethylene complex **7** and HOTf. **(B) In CD_2Cl_2 :** A procedure similar to A was followed in CD_2Cl_2 and the reaction was found to take 6-12 h to reach completion to produce **7** and HOTf (~ δ 13.5). $\sim\text{NET}_2$ (~ 6 mg) was added and the HOTf signal at ~ δ 13.5 (br) disappeared. After ~ 20 min $(\text{COD})\text{Pt}(\text{Et})(\text{OTf})$ (**6**) appeared. Characteristic signals for (**6**): ^1H NMR (AMX-300, CD_2Cl_2): 5.81 (m, $J_{\text{Pt-H}} = 24.5$ Hz) 4.41 (m, $J_{\text{Pt-H}} = 97.5$ Hz), 1.54 (overlapped), 0.89 (t).

Observation of $[(\text{COD})\text{Pt}(\text{OH})]_2[\text{OTf}]_2$ (4**) from $(\text{COD})\text{Pt}(\text{OTf})_2 + 10$ eq H_2O :** Inside the dry box $(\text{COD})\text{Pt}(\text{OTf})_2$ (4.5 mg, 0.0075 mmol) was measured into a NMR tube and dissolved in 0.45 mL CD_2Cl_2 . The tube was taken out from the drybox, the NMR cap opened and de-ionized H_2O (1.5 μL , 0.083 mmol) added and mixed well by shaking. ^1H and ^{195}Pt NMR spectroscopy displayed that **4** has formed. Characteristic signals for **4**: ^1H NMR (AMX-300, CD_2Cl_2): 5.67 (s, br with Pt satellites) ^{195}Pt NMR (64 MHz, CD_2Cl_2): -2762

$(\text{COD})\text{Pt}(\text{OTf})_2 + 1$ equivalent of $\text{H}_2\text{O} + \text{C}_2\text{H}_4$: Outside the drybox corannulene (1.0 mg, 0.0039 mmol) was added to a screw cap NMR tube and the tube was taken inside the drybox. $(\text{COD})\text{Pt}(\text{OTf})_2$ (5.0 mg, 0.0083 mmol) was added and the solids dissolved in 0.50 mL CD_2Cl_2 . The tube was taken out from the dry box. The screw cap was opened and de-ionized H_2O (15.0 μL from a solution of 990 μL of CDCl_3 and 10 μL H_2O) was added and mixed well by shaking. Ethylene (4.0 mL, 16.0 mmol) was added via the screw cap septum and the contents were well mixed by shaking. The reaction was monitored by ^1H NMR spectroscopy. (300-AMX)

$(\text{COD})\text{Pt}(\text{OTf})_2 + \text{H}_2\text{O} + \text{C}_2\text{H}_4$: The following experiments were performed from a same batch of $(\text{COD})\text{Pt}(\text{OTf})_2$ and same stock solvent of CD_2Cl_2 . The amount of H_2O was varied from 20 equivalents, 10 equivalents to 5 equivalents. **(A) 20 equivalents of H_2O :** Corannulene (1.0 mg, 0.0039 mmol) was added to a screw cap NMR tube and the

tube was taken into the drybox. (COD)Pt(OTf)₂ (5.0 mg, 0.0083 mmol) was added and the solids were dissolved in 0.45 mL CD₂Cl₂. The sealed tube was taken outside the drybox, opened and de-ionized H₂O (3.0 µL, 0.17 mmol) was added and mixed well. The NMR tube was placed in dry ice/acetone bath and ethylene (4.0 mL, 0.16 mmol) was added via the screw cap septum. The tube was taken out from the bath and mixed well by shaking and immediately placed in 300-AMX probe at ambient temperature. The reaction was measured by ¹H NMR spectroscopy. **(B) 10 equivalents of H₂O:** A procedure similar to above was followed to produce a CD₂Cl₂ solution of (COD)Pt(OTf)₂ (5.0 mg, 0.0083 mmol) and corannulene (1.3 mg, 0.0052 mmol) followed by the addition of de-ionized H₂O (1.5 µL, 0.083 mmol). Ethylene addition and reaction monitoring were also performed similar to the procedure described above. **(C) 5 equivalents of H₂O:** A procedure similar to above was followed to monitor a reaction of corannulene (1.4 mg, 0.0056 mmol), (COD)Pt(OTf)₂ (5.0 mg, 0.0083 mmol) de-ionized H₂O (0.8 µL, 0.044 mmol) and ethylene (4.0 mL, 0.16 mmol) in 0.45 mL CD₂Cl₂.

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