Platinum(II) Enyne Cycloisomerization Catalysis: Intermediates and Resting States

Supporting Information

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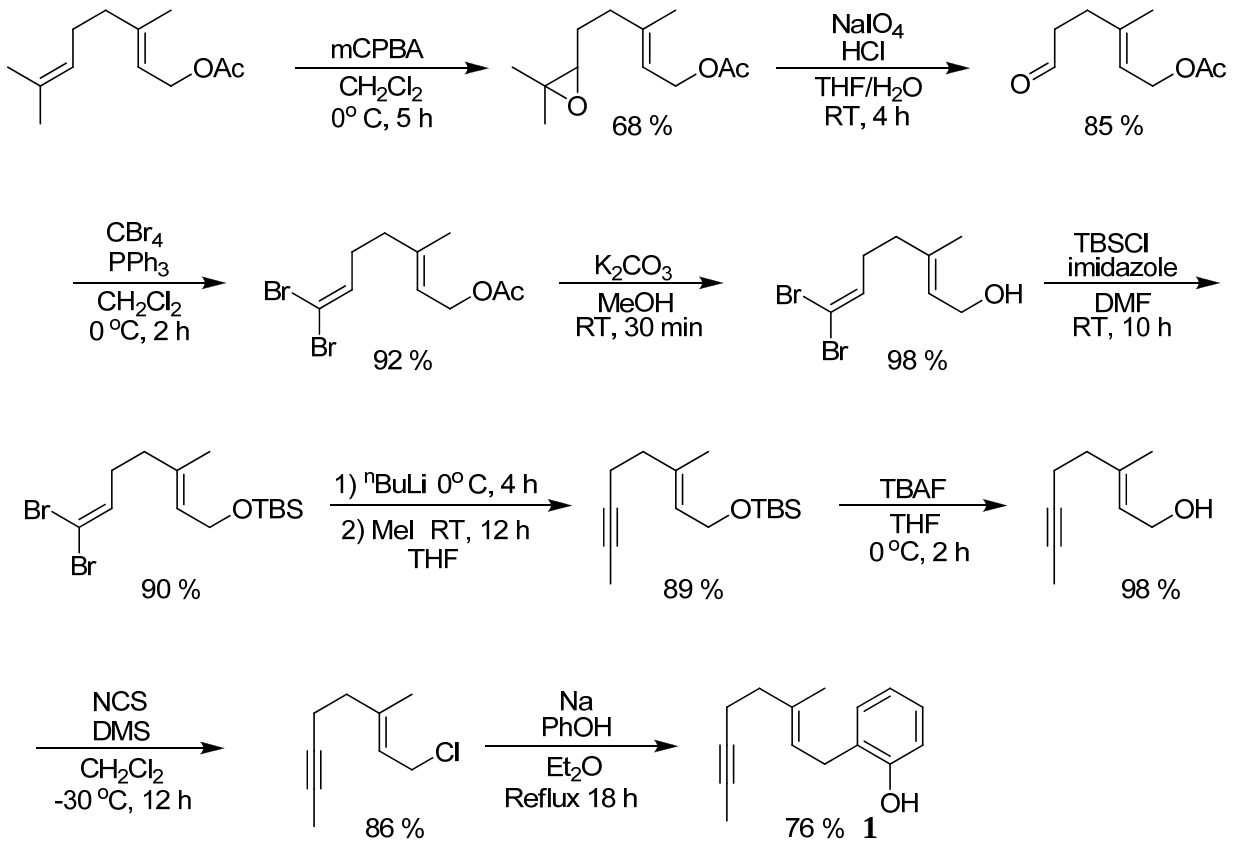
General Procedures

Synthetic procedures were carried out under nitrogen using standard Schlenk techniques or in a nitrogen filled glove box. CD_2Cl_2 and CD_3NO_2 were distilled from CaH_2 and freeze-pump-thaw degassed before use. $MeNO_2$ was purified as previously described [1] and distilled from CaH_2. TriPHOS, dppe, and BINAP were purchased from Aldrich and used as received. (*S*)-Me-SoniPHOS and (*S*)-MeOBIPHEP were purchased from Strem and used as received. The piperidinomethyl polystyrene resin was purchased from NovaBiochem. $(COD)PtI_2$,[2] $(P_2)(PMe_3)PtI_2$,[3] $(PPP)PtI_2$, and $[(PPP)Pt(NCC_6F_5)][BF_4]_2$[4] were prepared according to literature procedures. NMR spectra were recorded on a Bruker 400 MHz Avance or Bruker 500 MHz Avance spectrometer; chemical shifts are reported in ppm and referenced to residual solvent peaks (^1H, ^{13}C) or to an external standard (85% H_3PO_4 for ^{31}P NMR). GC was performed on an HP-6890. Elemental microanalyses were performed by Robertson-Microlit Laboratories, Madison, NJ. High-resolution mass spectrometry was performed by the mass spectrometry service laboratory at the University of Illinois.

Synthesis of 1: The (2E)-7,7-Dibromo-3-methylhepta-2,6-dien-1-ol was obtained following a modified procedure established by Malacria.[5] The substrate was protected with a TBS group, followed by a Corey-Fuchs to the methyl alkyne. Cleavage of the TBS group with TBAF generated the free alcohol, which was converted to the

allyl chloride with treatment of NCS/DMS. Nucleophilic displacement of the chloride with sodium phenoxide yielded the desired product (**1**) (E)-2-(3-methyloct-2-en-6-ynyl)phenol.



(E)-2-(3-methyloct-2-en-6-ynyl)phenol (1) was isolated as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) 7.10 (t, *J* = 7.6 Hz, 2H), 6.84 (t, *J* = 7.6Hz, 1 H), 6.79 (d, *J* = 7.6Hz, 1H), 5.37 (t, *J* = 6.8 Hz, 1H), 5.04 (s, 1H), 3.36 (d, 7.2 *J* = Hz, 2H), 2.27-2.18 (m, 4H), 1.75 (s, 6H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 154.2, 136.3, 129.7, 127.2, 127.0, 122.8, 120.5, 115.6, 78.5, 76.3, 38.7, 29.2, 17.5, 15.6, 3.3. HRMS (ESI+) *m*/*z* $[M+H]^+$: observed 215.1234, calculated. 215.1436 for $C_{15}H_{18}O$.

(E)-2-(3-methylhept-2-en-6-ynyl)phenol (5) was prepared analogously to **1** and isolated as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.01 (t, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.42 (td, *J* = 8.0 and 1.0 Hz, 1H), 5.04 (s, 1H), 3.40 (d, *J* = 7.1 Hz, 2H), 2.37-2.27 (m, 4H), 1.98 (t, *J* = 2.5 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 154.1, 136.1, 129.9, 127.4, 126.8, 123.1, 120.7, 115.7, 83.8, 68.9, 38.2, 29.4, 17.3, 15.8. HRMS (EI+) *m*/*z* $[M]^+$: observed 200.1199, calcd. 200.1201 for $C_{14}H_{16}O$.

General Procedure for Isolation of Pt-alkenyls.

To a solution of $[(PPP)Pt(NCC_6F_5)][BF_4]_2$ (0.60 mmol) and piperidinomethyl polystyrene resin (1.20 mmol) in CH_2Cl_2 was added enyne (**1** or **5**) (0.70 mmol). The solution was allowed to stir for 15 min in air then the basic resin was filtered off and the Pt-alkenyl precipitated with Et_2O.

(PPP)Pt-alkenyl (3). After following the procedure described above, the resulting white solid was washed with Et_2O, dissolved in CH_2Cl_2 and diluted with Et_2O. The solvent was allowed to evaporate, yielding colorless needles (95 %). The NMRs for this complex were taken at -68 °C. $^1H\{^{31}P\}$ NMR: (400 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.51-7.45 (m, 8H), 7.32-7.19 (m, 13H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 6. 60 (t, *J* = 8.0 Hz, 1H), 3.45 (b, 2H), 2.87 (b, 2H), 2.55 (b, 4H), 2.11 (b, 2H), 2.08 (m, 2H), 1.80, (s, 2H), 1.52 (m, 1), 0.77 (s, 3H), -0.33(s, 3H). $^{31}P\{^1H\}$ NMR: (162 MHz, $CDCl_3$). δ 88.09 (s, $J_{Pt\text{-}P}$ = 1398 Hz, 1P), 39.79 (s, $J_{Pt\text{-}P}$ = 2775 Hz, 2P). HRMS (ESI+) *m*/*z* $[M]^+$: observed 941.2664, calcd. 941.2701 for $C_{49}H_{50}OP_3Pt$.

(PPP)Pt-alkenyl (6). After following the procedure described above, the resulting solid was washed with Et_2O and dried in vacuo yielding desired product in 97 %. $^1H\{^{31}P\}$ NMR: (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.50-7.42 (m, 21H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 1H), 6. 66 (t, *J* = 8.0 Hz, 1H), 4.59 (d, *J* = 12 Hz, $J_{Pt\text{-}H}$ = 44.0 Hz, 1H) 3.24 (b, 2H), 2.93 (m, 2H), 2.53 (m, 4H), 2.11 (m, 2H), 2.08 (m, 2H), 2.01 (m, 1H), 1.41 (m, 1H), 1.33(m, 1H), 0.55 (s, 3H). $^{31}P\{^1H\}$ NMR: (162 MHz, $CDCl_3$). δ 89.82 (s, $J_{Pt\text{-}P}$ = 1438 Hz, 1P), 38.52 (s, $J_{Pt\text{-}P}$ = 2812 Hz, 2P). HRMS (ESI+) *m*/*z* $[M]^+$: observed 927.2545, calcd. 927.2511 for $C_{48}H_{48}OP_3Pt$.

General Procedure for Catalysis.

To a solution of $(PPP)PtI_2$ (0.30 mmol) in CD_3NO_2 was added $AgBF_4$ (0.60 mmol). The reaction was stirred for 1 h, then the catalyst was filtered away from the silver salts via a PTFE syringe filter into a solution of **1** or **5** (1.5 mmol) and Ph_2NMe (0.45 mmol) in CD_3NO_2. The reaction was monitored by ^{31}P and ^1H NMR. Once the substrate was consumed the product was extracted with 1 mL pentane (2x). The pentane was removed via rotary evaporation to yield the isolated product.

1,4a-dimethyl-4,4a,9,9a-tetrahydro-3H-xanthene (2) was prepared as described above and isolated as a colorless oil in 87 % yield. ^1H NMR: (400 MHz, $CDCl_3$) δ 7.12-7.07 (m, 2H), 6.82 (td, *J* = 8.4 and 2.8 Hz, 2H), 5.38 (s, 1H), 2.86 (m, 1H), 2.52 (m, 2H), 2.17 (m, 2H), 1.96-1.82 (m, 2H), 1.52 (s, 3H), 1.10 (s, 3H). δ ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.7, 133.6, 129.8, 127.4, 122.5, 121.5, 119.7, 117.4, 76.0, 42.0, 35.5, 25.9, 24.1, 19.8, 16.6. HRMS (ESI+) *m*/*z* $[M+H]^+$: observed 215.1234, calcd. 215.1436 for $C_{15}H_{19}O$.

4a-methyl-4,4a,9,9a-tetrahydro-1H-xanthene (7) was prepared as described above and isolated as a colorless oil in 96 % yield. ^1H and ^{13}C NMR matched previously reported data.[6]

General Procedure for Protonolysis/Deuterolysis of Pt-alkenyl

To a solution of **3** or **6** in CH_2Cl_2/CD_2Cl_2 was added HBF_4 as a solution in Et_2O and CH_3OH/CD_3OD. The reaction stirred for 10 min. Solution was then washed with H_2O/D_2O, extracted with pentane, dried over $MgSO_4$, and filtered. The solvent was removed via rotary evaporation yielding the desired product.

1,4a-dimethyl-4,4a,9,9a-tetrahydro-3H-xanthene (2) was isolated as a colorless oil in 96 % yield; ^1H and ^{13}C NMR matched above spectra.

4a-methyl-4,4a,9,9a-tetrahydro-1H-xanthene (7) was isolated as a colorless oil in 95 % yield; ^1H and ^{13}C NMR matched previously reported data.[6]

2-d_1: was isolated as a colorless oil in 96 % yield. ^1H NMR: (400 MHz, $CDCl_3$) δ 7.07 (m, 2H), 6.81 (m, 2H), 2.86 (m, 1H), 2.50 (m, 2H), 2.19 (m, 2H), 1.92 (m, 2H), 1.71 (s, 3H), 1.10 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.6, 133.5, 129.9, 127.5, 122.5, 121.5 (C-D), 119.7, 117.4, 76.1, 41.9, 35.5, 25.9, 24.0, 19.8, 16.6. ^2H NMR: (500 MHz, $CHCl_3$) δ 5.42 (s, 1D). HRMS (EI+) *m*/*z* $[M]^+$: observed 215.1423, calcd. 215.1420 for $C_{14}H_{17}DO$.

7-d_2: was isolated as a colorless oil in 94 % yield. ^1H NMR: (400 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.82 (m, 2H), 5.49 (s, 1H), 2.71 (d, *J* = 4.0 Hz, 1H), 2.48 (m, 3.5H), 2.13 (m, 1H), 1.78 (m, 0.5H), 1.10 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.9, 129.7, 127.2, 125.5 (C-D), 125.3, 125.1, 120.0, 117.0, 76.0, 39.9, 34.2, 31.8 (C-D), 31.1, 16.1. ^2H NMR: (500 MHz, $CHCl_3$) δ 5.49 (s, 1D), 2.36 (s, 0.5D), 1.77 (s, 0.5D). HRMS (EI+) *m*/*z* $[M]^+$: observed 202.1325, calcd. 202.1327 for $C_{14}H_{14}D_2O$.

General Procedure for Reductive Cleavage of Organic Fragment.

To a solution of **3** or **6** in THF at 0 °C was added $LiHBEt_3$ in THF. The reaction was stirred for 30 min. Solvent was removed via rotary evaporation and the product was extracted with pentane and filtered through celite. The solvent was then removed via rotary evaporation to yield the desired product.

4a-methyl-4,4a,9,9a-tetrahydro-3H-xanthene (8) was isolated as a colorless oil in 89 % yield. ^1H NMR: (400 MHz, $CDCl_3$) δ 7.07 (m, 2H), 6.82 (t, *J* = 9.6 Hz, 2H), 5.65 (d, *J* = 12.8 Hz, 1H), 5.47 (d, *J* = 12.8 Hz, 1H), 2.69 (d, *J* = 14.0 Hz, 1H), 2.52 (m, 2H), 2.22 (m, 3H), 1.91 (m, 2H), 1.14 (s, 3H). δ ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.2, 132.9, 130.1, 127.7, 122.7, 122.0, 119.3, 118.4, 75.2, 42.7, 35.5, 24.5, 19.6, 15.6. HRMS (EI+) *m*/*z* $[M]^+$: observed 200.1204, calcd. 200.1201 for $C_{14}H_{16}O$.

4a-methyl-4,4a,9,9a-tetrahydro-1H-xanthene (7) was isolated as a colorless oil in 87 % yield. ^1H and ^{13}C NMR matched previously reported data.[6]

X-ray Structure Determinations.

Crystals of **3** suitable for X-ray crystallography were grown from a sample of **3** in a solution of CH_2Cl_2 and *n*-pentane. Single crystals were mounted on the ends of a fiber. Intensity data were collected on a Siemens SMART diffractometer with CCD detection using Mo Kα radiation of wavelength 0.71073 Å (to scan mode). The structure was solved by direct methods and refined by least squares techniques on *F* using structure solution programs from the NARCVAX system.[7] Phenyl ring thermal parameters and geometries had to be constrained due to a large portion of weak reflections. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions (C-H = 0.96 Å) and allowed to ride on the atoms to which they were bonded. Crystal data, data collection and the refinement parameters for **3** are listed in Table S1. Absorption corrections were made using SADABS.

Table S1. Crystallographic data and collection parameters for **3.**

	3
Empirical Formula	$C_{49}H_{50}BF_4OP_3Pt$
FW	1029.70
Space group	Monoclinic, $P2_1/c$
A	10.4824(8)
B	23.673(2)
C	18.98784(16)
V, Å^3	4538.5(7)
Z	4
T, K	100(2)
D_c, Mg/m^3	1.507
λ, Å	0.71073
μ, mm^{-1}	3.249
R_f[a]	0.1271
R_w[b]	0.2707
GOF[c]	1.111

[a] $R_f = \Sigma(F_o - F_c)/\Sigma F_o$ [b] $R_w = [\Sigma\omega(Fo - F_c)^2/\Sigma\omega F_o^2]^{1/2}$ [c] $GOF = [\Sigma\omega(F_o - F_c)^2/(n\text{-}p)]^{1/2}$, where n = number of reflections and p = number of parameters.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	2711(1)	9200(1)	2747(1)	57(1)
P(1)	4759(5)	9253(3)	3523(3)	55(2)
P(2)	2001(5)	9177(3)	3792(4)	62(2)

P(3)	560(5)	9372(3)	2172(4)	69(2)
C(1)	3301(16)	9198(9)	1763(11)	38(5)
C(2)	3580(20)	9762(9)	1436(12)	52(6)
C(3)	3510(20)	9732(10)	613(13)	58(7)
C(4)	4290(20)	9242(11)	481(12)	58(6)
O(5)	4259(14)	9241(7)	-294(9)	62(4)
C(6)	4600(20)	8748(11)	-581(14)	54(6)
C(7)	4800(20)	8799(12)	-1301(13)	59(7)
C(8)	5140(20)	8316(13)	-1609(14)	67(7)
C(9)	5280(20)	7832(13)	-1285(16)	70(8)
C(10)	5120(20)	7773(11)	-579(16)	69(8)
C(11)	4790(20)	8255(12)	-239(14)	64(7)
C(12)	4470(20)	8186(10)	535(14)	64(7)
C(13)	3640(20)	8708(10)	645(13)	57(6)
C(14)	3296(19)	8726(10)	1379(15)	58(7)
C(15)	5730(20)	9302(10)	893(13)	61(7)
C(16)	2980(20)	8149(12)	1651(14)	74(8)
C(17)	6035(7)	8730(4)	3465(6)	62(6)
C(18)	6100(10)	8519(4)	2787(6)	69(6)
C(19)	7072(12)	8132(4)	2739(8)	81(7)
C(20)	7979(10)	7955(4)	3369(9)	97(9)
C(21)	7915(11)	8165(4)	4046(8)	96(9)
C(22)	6943(11)	8552(4)	4095(6)	89(8)
C(23)	5514(8)	9949(4)	3489(5)	51(5)
C(24)	6852(8)	9977(4)	3476(5)	84(9)
C(25)	7378(10)	10516(4)	3456(8)	100(11)
C(26)	6625(12)	11029(4)	3462(8)	71(7)
C(27)	5282(11)	10948(4)	3464(7)	72(7)
C(28)	4708(9)	10433(4)	3472(7)	63(6)
C(29)	4560(20)	9218(12)	4464(11)	63(7)
C(30)	3260(30)	9478(12)	4529(14)	80(8)
C(31)	1787(14)	8489(5)	4122(10)	65(6)
C(32)	1326(14)	8430(7)	4748(9)	75(6)
C(33)	1124(15)	7895(9)	5002(8)	100(8)
C(34)	1383(16)	7419(6)	4631(12)	97(9)
C(35)	1844(17)	7478(6)	4005(11)	105(10)
C(36)	2046(15)	8013(7)	3750(9)	77(7)
C(37)	370(20)	9500(12)	3610(14)	66(7)
C(38)	-390(20)	9293(13)	2870(17)	90(10)
C(39)	-258(10)	9003(5)	1289(9)	151(9)
C(40)	-663(16)	8472(5)	1457(11)	152(9)
C(41)	-1296(15)	8110(6)	900(13)	155(9)
C(42)	-1523(14)	8281(7)	174(12)	162(9)
C(43)	-1118(16)	8812(8)	6(10)	161(9)
C(44)	-485(12)	9174(6)	564(8)	159(9)
C(45)	329(10)	10155(5)	1924(6)	77(7)
C(46)	-1010(10)	10388(5)	1554(7)	86(8)
C(47)	-1073(14)	10971(5)	1457(9)	111(11)
C(48)	8(16)	11307(5)	1813(9)	141(15)
C(49)	1232(14)	11090(6)	2178(10)	131(14)
C(50)	1356(12)	10497(6)	2249(8)	93(9)
B(1)	1230(20)	3907(11)	9160(13)	113(9)
F(1)	1550(40)	3352(10)	9232(16)	239(14)
F(2)	2320(20)	4126(14)	9008(18)	230(13)
F(3)	920(30)	4214(13)	9700(14)	212(11)
F(4)	230(20)	3944(14)	8553(14)	209(12)

Table S3. Bond lengths [Å] and angles [°] for 3.

Pt(1)-C(1)	2.10(2)	C(39)-C(40)	1.3900
Pt(1)-P(2)	2.275(6)	C(39)-C(44)	1.3900
Pt(1)-P(1)	2.283(6)	C(40)-C(41)	1.3900
Pt(1)-P(3)	2.284(6)	C(41)-C(42)	1.3900
P(1)-C(23)	1.835(11)	C(42)-C(43)	1.3900
P(1)-C(29)	1.84(2)	C(43)-C(44)	1.3900
P(1)-C(17)	1.846(11)	C(45)-C(50)	1.3648
P(2)-C(31)	1.777(14)	C(45)-C(46)	1.5091
P(2)-C(30)	1.81(3)	C(46)-C(47)	1.3913
P(2)-C(37)	1.82(2)	C(47)-C(48)	1.4115
P(3)-C(38)	1.85(2)	C(48)-C(49)	1.3956
P(3)-C(39)	1.889(16)	C(49)-C(50)	1.4141
P(3)-C(45)	1.913(15)	B(1)-F(4)	1.348(10)
C(1)-C(14)	1.33(3)	B(1)-F(2)	1.351(10)
C(1)-C(2)	1.53(3)	B(1)-F(1)	1.354(10)
C(2)-C(3)	1.54(3)	B(1)-F(3)	1.355(10)
C(3)-C(4)	1.48(3)	C(1)-Pt(1)-P(2)	177.6(5)
C(4)-O(5)	1.45(2)	C(1)-Pt(1)-P(1)	97.6(5)
C(4)-C(13)	1.51(3)	P(2)-Pt(1)-P(1)	84.4(2)
C(4)-C(15)	1.52(3)	C(1)-Pt(1)-P(3)	93.0(5)
O(5)-C(6)	1.37(3)	P(2)-Pt(1)-P(3)	85.4(2)
C(6)-C(11)	1.33(3)	P(1)-Pt(1)-P(3)	162.9(3)
C(6)-C(7)	1.43(3)	C(23)-P(1)-C(29)	103.1(9)
C(7)-C(8)	1.37(3)	C(23)-P(1)-C(17)	106.0(4)
C(8)-C(9)	1.29(3)	C(29)-P(1)-C(17)	106.5(9)
C(9)-C(10)	1.39(3)	C(23)-P(1)-Pt(1)	111.8(4)
C(10)-C(11)	1.39(3)	C(29)-P(1)-Pt(1)	107.7(7)
C(11)-C(12)	1.59(3)	C(17)-P(1)-Pt(1)	120.4(4)
C(12)-C(13)	1.55(3)	C(31)-P(2)-C(30)	102.8(11)
C(13)-C(14)	1.52(3)	C(31)-P(2)-C(37)	104.9(10)
C(14)-C(16)	1.52(3)	C(30)-P(2)-C(37)	116.6(12)
C(17)-C(18)	1.3900	C(31)-P(2)-Pt(1)	115.0(7)
C(17)-C(22)	1.3900	C(30)-P(2)-Pt(1)	109.1(9)
C(18)-C(19)	1.3900	C(37)-P(2)-Pt(1)	108.6(8)
C(19)-C(20)	1.3900	C(38)-P(3)-C(39)	112.1(11)
C(20)-C(21)	1.3900	C(38)-P(3)-C(45)	102.4(10)
C(21)-C(22)	1.3900	C(39)-P(3)-C(45)	103.3(7)
C(23)-C(24)	1.4109	C(38)-P(3)-Pt(1)	106.6(9)
C(23)-C(28)	1.4206	C(39)-P(3)-Pt(1)	121.0(4)
C(24)-C(25)	1.3950	C(45)-P(3)-Pt(1)	109.8(4)
C(25)-C(26)	1.4479	C(14)-C(1)-C(2)	119.1(19)
C(26)-C(27)	1.4215	C(14)-C(1)-Pt(1)	121.5(17)
C(27)-C(28)	1.3596	C(2)-C(1)-Pt(1)	119.0(14)
C(29)-C(30)	1.53(3)	C(1)-C(2)-C(3)	113.6(17)
C(31)-C(32)	1.3900	C(4)-C(3)-C(2)	108.3(19)
C(31)-C(36)	1.3900	O(5)-C(4)-C(3)	107(2)
C(32)-C(33)	1.3900	O(5)-C(4)-C(13)	107.8(18)
C(33)-C(34)	1.3900	C(3)-C(4)-C(13)	108.8(17)
C(34)-C(35)	1.3900	O(5)-C(4)-C(15)	106.7(16)
C(35)-C(36)	1.3900	C(3)-C(4)-C(15)	111(2)
C(37)-C(38)	1.51(4)	C(13)-C(4)-C(15)	115(2)

C(6)-O(5)-C(4)	117.1(19)	C(30)-C(29)-P(1)	112.1(17)
C(11)-C(6)-O(5)	125(2)	C(29)-C(30)-P(2)	105.9(17)
C(11)-C(6)-C(7)	120(2)	C(32)-C(31)-C(36)	120.0
O(5)-C(6)-C(7)	115(2)	C(32)-C(31)-P(2)	119.4(11)
C(8)-C(7)-C(6)	117(2)	C(36)-C(31)-P(2)	120.6(11)
C(9)-C(8)-C(7)	124(3)	C(31)-C(32)-C(33)	120.0
C(8)-C(9)-C(10)	121(2)	C(34)-C(33)-C(32)	120.0
C(9)-C(10)-C(11)	118(3)	C(33)-C(34)-C(35)	120.0
C(6)-C(11)-C(10)	121(3)	C(34)-C(35)-C(36)	120.0
C(6)-C(11)-C(12)	120(2)	C(35)-C(36)-C(31)	120.0
C(10)-C(11)-C(12)	118(3)	C(38)-C(37)-P(2)	107.1(16)
C(13)-C(12)-C(11)	107(2)	C(37)-C(38)-P(3)	111.8(16)
C(4)-C(13)-C(14)	112.8(19)	C(40)-C(39)-C(44)	120.0
C(4)-C(13)-C(12)	110.2(18)	C(40)-C(39)-P(3)	108.3(5)
C(14)-C(13)-C(12)	114(2)	C(44)-C(39)-P(3)	131.7(5)
C(1)-C(14)-C(13)	123(2)	C(41)-C(40)-C(39)	120.0
C(1)-C(14)-C(16)	123(2)	C(40)-C(41)-C(42)	120.0
C(13)-C(14)-C(16)	114(2)	C(43)-C(42)-C(41)	120.0
C(18)-C(17)-C(22)	120.0	C(42)-C(43)-C(44)	120.0
C(18)-C(17)-P(1)	119.7(5)	C(43)-C(44)-C(39)	120.0
C(22)-C(17)-P(1)	120.3(5)	C(50)-C(45)-C(46)	122.1
C(19)-C(18)-C(17)	120.0	C(50)-C(45)-P(3)	115.2(5)
C(18)-C(19)-C(20)	120.0	C(46)-C(45)-P(3)	121.0(5)
C(21)-C(20)-C(19)	120.0	C(47)-C(46)-C(45)	115.6
C(20)-C(21)-C(22)	120.0	C(46)-C(47)-C(48)	119.4
C(21)-C(22)-C(17)	120.0	C(49)-C(48)-C(47)	124.0
C(24)-C(23)-C(28)	123.3	C(48)-C(49)-C(50)	117.7
C(24)-C(23)-P(1)	118.8(3)	C(45)-C(50)-C(49)	120.2
C(28)-C(23)-P(1)	117.8(3)	F(4)-B(1)-F(2)	108(2)
C(25)-C(24)-C(23)	116.4	F(4)-B(1)-F(1)	106(3)
C(24)-C(25)-C(26)	123.2	F(2)-B(1)-F(1)	101(3)
C(27)-C(26)-C(25)	115.4	F(4)-B(1)-F(3)	109(2)
C(28)-C(27)-C(26)	124.2	F(2)-B(1)-F(3)	109(3)
C(27)-C(28)-C(23)	117.5	F(1)-B(1)-F(3)	123(3)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	32(1)	80(1)	65(1)	1(1)	22(1)	-3(1)
P(1)	37(3)	82(5)	50(4)	8(4)	19(3)	-4(3)
P(2)	42(3)	79(5)	74(5)	3(4)	33(3)	1(3)
P(3)	27(3)	114(6)	73(5)	-6(4)	23(3)	-6(3)
C(1)	29(9)	32(12)	51(13)	-10(12)	4(9)	-11(10)
C(2)	49(13)	49(15)	63(17)	-18(12)	24(12)	-9(11)
C(3)	72(16)	57(16)	55(17)	13(13)	30(13)	7(13)
C(4)	73(15)	63(16)	52(15)	-15(14)	40(12)	-14(14)
O(5)	61(9)	55(11)	75(12)	5(10)	23(8)	-22(9)
C(6)	47(13)	43(16)	75(19)	1(14)	21(12)	3(11)
C(7)	53(13)	90(20)	46(15)	-4(14)	28(12)	7(13)
C(8)	73(17)	80(20)	46(16)	11(16)	13(13)	1(15)

C(9)	62(15)	80(20)	80(20)	-33(18)	51(15)	-4(14)
C(10)	48(13)	64(18)	110(20)	-4(16)	42(15)	3(12)
C(11)	38(12)	90(20)	69(18)	-18(17)	17(12)	5(13)
C(12)	67(15)	50(16)	80(20)	-16(14)	37(14)	0(12)
C(13)	38(12)	66(17)	68(18)	4(13)	14(12)	0(11)
C(14)	34(11)	42(15)	110(20)	1(15)	30(13)	1(10)
C(15)	67(15)	59(17)	71(17)	4(13)	41(13)	-16(12)
C(16)	50(14)	120(20)	67(18)	-11(16)	31(13)	-21(15)
C(17)	17(9)	89(18)	78(14)	4(12)	12(9)	-16(9)
C(18)	36(11)	94(19)	82(13)	12(14)	25(11)	8(10)
C(19)	53(14)	100(20)	101(15)	28(15)	29(12)	28(13)
C(20)	22(10)	170(30)	109(18)	64(16)	32(12)	3(13)
C(21)	36(13)	130(30)	112(15)	28(19)	-9(14)	-9(11)
C(22)	44(13)	110(20)	96(14)	17(15)	-11(12)	-16(12)
C(23)	28(8)	92(13)	31(12)	-4(12)	-1(9)	-8(8)
C(24)	49(11)	78(12)	140(30)	-1(18)	47(16)	-6(10)
C(25)	67(15)	91(14)	170(30)	0(20)	80(20)	-14(10)
C(26)	60(12)	76(12)	77(18)	3(15)	18(14)	-21(10)
C(27)	54(11)	95(13)	69(17)	9(15)	20(13)	-2(10)
C(28)	30(10)	94(15)	63(16)	20(15)	8(11)	-1(8)
C(29)	48(12)	100(20)	42(13)	12(15)	17(10)	-19(14)
C(30)	100(20)	90(20)	58(18)	-3(15)	27(16)	28(17)
C(31)	12(9)	80(13)	99(18)	-10(12)	5(10)	8(10)
C(32)	38(12)	89(14)	89(18)	6(14)	0(12)	2(13)
C(33)	49(15)	110(18)	130(20)	36(16)	0(16)	4(17)
C(34)	43(14)	81(14)	160(30)	45(17)	15(16)	-1(14)
C(35)	59(16)	71(12)	190(30)	28(16)	50(20)	3(15)
C(36)	65(16)	54(13)	110(20)	8(12)	15(15)	11(13)
C(37)	36(12)	110(20)	67(18)	2(16)	35(12)	10(13)
C(38)	42(13)	110(30)	130(30)	10(20)	52(16)	11(15)
C(39)	72(11)	240(20)	163(19)	-65(19)	79(13)	-7(13)
C(40)	72(12)	240(20)	168(19)	-69(18)	82(13)	-9(13)
C(41)	74(11)	240(20)	171(19)	-72(19)	76(13)	-8(13)
C(42)	76(12)	240(20)	180(19)	-71(19)	57(14)	-6(13)
C(43)	80(12)	240(20)	174(19)	-71(19)	56(14)	1(13)
C(44)	82(12)	250(20)	168(19)	-67(19)	63(14)	-1(13)
C(45)	39(10)	116(17)	80(20)	17(15)	21(12)	2(10)
C(46)	55(11)	116(17)	90(20)	7(18)	16(12)	13(13)
C(47)	98(18)	99(18)	130(30)	-37(19)	12(18)	29(15)
C(48)	110(20)	105(19)	180(40)	-10(30)	-30(20)	23(14)
C(49)	74(16)	95(14)	220(40)	-20(30)	26(19)	28(15)
C(50)	57(13)	97(15)	120(30)	-7(19)	11(14)	7(13)
B(1)	62(18)	140(20)	130(30)	30(20)	25(14)	0(20)
F(1)	390(40)	121(17)	180(30)	22(16)	20(20)	1(17)
F(2)	108(14)	300(30)	300(30)	50(30)	70(16)	-80(20)
F(3)	250(30)	250(30)	145(18)	2(19)	56(18)	60(30)
F(4)	92(12)	340(30)	170(20)	-40(20)	-15(14)	48(18)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for **3.**

	x	y	z	U(eq)

H(2A)	4474	9891	1696	62
H(2B)	2943	10046	1519	62
H(3A)	2578	9687	333	70
H(3B)	3855	10084	451	70
H(7)	4698	9150	-1553	70
H(8)	5269	8339	-2088	80
H(9)	5507	7511	-1532	84
H(10)	5236	7418	-337	82
H(12A)	3964	7835	549	77
H(12B)	5294	8169	926	77
H(13)	2789	8679	266	68
H(15A)	6273	9041	686	92
H(15B)	5832	9213	1410	92
H(15C)	6026	9691	846	92
H(16A)	3796	7930	1812	112
H(16B)	2372	7947	1254	112
H(16C)	2574	8198	2061	112
H(18)	5480	8640	2357	83
H(19)	7116	7989	2276	98
H(20)	8643	7691	3336	116
H(21)	8535	8044	4477	115
H(22)	6899	8696	4558	106
H(24)	7368	9646	3480	101
H(25)	8272	10550	3438	120
H(26)	7003	11394	3465	85
H(27)	4752	11274	3460	86
H(28)	3803	10400	3465	76
H(29A)	4600	8818	4623	76
H(29B)	5300	9421	4794	76
H(30A)	3277	9894	4482	96
H(30B)	3083	9383	5008	96
H(32)	1149	8756	5002	90
H(33)	809	7855	5430	120
H(34)	1245	7053	4804	116
H(35)	2021	7152	3751	126
H(36)	2361	8053	3323	93
H(37A)	-78	9389	3991	79
H(37B)	450	9917	3610	79
H(38A)	-1221	9509	2717	108
H(38B)	-618	8890	2907	108
H(40)	-507	8355	1952	183
H(41)	-1572	7747	1014	186
H(42)	-1956	8034	-206	194
H(43)	-1274	8929	-489	194
H(44)	-209	9537	449	191
H(46)	-1761	10153	1396	103
H(47)	-1837	11141	1154	133
H(48)	-104	11706	1803	170
H(49)	1957	11333	2372	157
H(50)	2156	10336	2524	112

Table S6. Torsion angles [°] for **3.**

C(1)-Pt(1)-P(1)-C(23)	70.9(7)	C(9)-C(10)-C(11)-C(12)	174(2)
P(2)-Pt(1)-P(1)-C(23)	-110.5(4)	C(6)-C(11)-C(12)-C(13)	14(3)
P(3)-Pt(1)-P(1)-C(23)	-56.9(9)	C(10)-C(11)-C(12)-C(13)	-159(2)
C(1)-Pt(1)-P(1)-C(29)	-176.6(11)	O(5)-C(4)-C(13)-C(14)	-165.0(18)
P(2)-Pt(1)-P(1)-C(29)	2.0(10)	C(3)-C(4)-C(13)-C(14)	-49(3)
P(3)-Pt(1)-P(1)-C(29)	55.7(13)	C(15)-C(4)-C(13)-C(14)	76(2)
C(1)-Pt(1)-P(1)-C(17)	-54.5(7)	O(5)-C(4)-C(13)-C(12)	66(2)
P(2)-Pt(1)-P(1)-C(17)	124.1(5)	C(3)-C(4)-C(13)-C(12)	-178(2)
P(3)-Pt(1)-P(1)-C(17)	177.8(7)	C(15)-C(4)-C(13)-C(12)	-53(3)
C(1)-Pt(1)-P(2)-C(31)	53(14)	C(11)-C(12)-C(13)-C(4)	-49(2)
P(1)-Pt(1)-P(2)-C(31)	-92.9(6)	C(11)-C(12)-C(13)-C(14)	-177.4(19)
P(3)-Pt(1)-P(2)-C(31)	100.8(6)	C(2)-C(1)-C(14)-C(13)	4(3)
C(1)-Pt(1)-P(2)-C(30)	167(14)	Pt(1)-C(1)-C(14)-C(13)	176.6(15)
P(1)-Pt(1)-P(2)-C(30)	21.8(10)	C(2)-C(1)-C(14)-C(16)	-178.0(19)
P(3)-Pt(1)-P(2)-C(30)	-144.4(10)	Pt(1)-C(1)-C(14)-C(16)	-5(3)
C(1)-Pt(1)-P(2)-C(37)	-65(14)	C(4)-C(13)-C(14)-C(1)	14(3)
P(1)-Pt(1)-P(2)-C(37)	149.9(10)	C(12)-C(13)-C(14)-C(1)	140(2)
P(3)-Pt(1)-P(2)-C(37)	-16.4(10)	C(4)-C(13)-C(14)-C(16)	-164.5(19)
C(1)-Pt(1)-P(3)-C(38)	171.1(12)	C(12)-C(13)-C(14)-C(16)	-38(3)
P(2)-Pt(1)-P(3)-C(38)	-7.1(11)	C(23)-P(1)-C(17)-C(18)	-92.3(6)
P(1)-Pt(1)-P(3)-C(38)	-60.6(14)	C(29)-P(1)-C(17)-C(18)	158.5(8)
C(1)-Pt(1)-P(3)-C(39)	41.5(9)	Pt(1)-P(1)-C(17)-C(18)	35.8(5)
P(2)-Pt(1)-P(3)-C(39)	-136.7(7)	C(23)-P(1)-C(17)-C(22)	86.7(7)
P(1)-Pt(1)-P(3)-C(39)	169.8(8)	C(29)-P(1)-C(17)-C(22)	-22.6(9)
C(1)-Pt(1)-P(3)-C(45)	-78.6(7)	Pt(1)-P(1)-C(17)-C(22)	-145.3(4)
P(2)-Pt(1)-P(3)-C(45)	103.2(5)	C(22)-C(17)-C(18)-C(19)	0.0
P(1)-Pt(1)-P(3)-C(45)	49.7(10)	P(1)-C(17)-C(18)-C(19)	178.9(4)
P(2)-Pt(1)-C(1)-C(14)	-41(15)	C(17)-C(18)-C(19)-C(20)	0.0
P(1)-Pt(1)-C(1)-C(14)	103.9(16)	C(18)-C(19)-C(20)-C(21)	0.0
P(3)-Pt(1)-C(1)-C(14)	-89.5(16)	C(19)-C(20)-C(21)-C(22)	0.0
P(2)-Pt(1)-C(1)-C(2)	131(14)	C(20)-C(21)-C(22)-C(17)	0.0
P(1)-Pt(1)-C(1)-C(2)	-83.5(14)	C(18)-C(17)-C(22)-C(21)	0.0
P(3)-Pt(1)-C(1)-C(2)	83.0(14)	P(1)-C(17)-C(22)-C(21)	-178.9(4)
C(14)-C(1)-C(2)-C(3)	14(3)	C(29)-P(1)-C(23)-C(24)	107.8(9)
Pt(1)-C(1)-C(2)-C(3)	-158.8(14)	C(17)-P(1)-C(23)-C(24)	-3.9(9)
C(1)-C(2)-C(3)-C(4)	-49(2)	Pt(1)-P(1)-C(23)-C(24)	-136.8(5)
C(2)-C(3)-C(4)-O(5)	-177.1(17)	C(29)-P(1)-C(23)-C(28)	-72.7(8)
C(2)-C(3)-C(4)-C(13)	67(2)	C(17)-P(1)-C(23)-C(28)	175.6(4)
C(2)-C(3)-C(4)-C(15)	-61(2)	Pt(1)-P(1)-C(23)-C(28)	42.6(4)
C(3)-C(4)-O(5)-C(6)	-162.3(18)	C(28)-C(23)-C(24)-C(25)	1.1
C(13)-C(4)-O(5)-C(6)	-45(2)	P(1)-C(23)-C(24)-C(25)	-179.5(5)
C(15)-C(4)-O(5)-C(6)	78(2)	C(23)-C(24)-C(25)-C(26)	1.1
C(4)-O(5)-C(6)-C(11)	10(3)	C(24)-C(25)-C(26)-C(27)	-2.1
C(4)-O(5)-C(6)-C(7)	-168.5(18)	C(25)-C(26)-C(27)-C(28)	1.0
C(11)-C(6)-C(7)-C(8)	2(3)	C(26)-C(27)-C(28)-C(23)	0.9
O(5)-C(6)-C(7)-C(8)	-180(2)	C(24)-C(23)-C(28)-C(27)	-2.1
C(6)-C(7)-C(8)-C(9)	0(4)	P(1)-C(23)-C(28)-C(27)	178.5(5)
C(7)-C(8)-C(9)-C(10)	-1(4)	C(23)-P(1)-C(29)-C(30)	87.4(19)
C(8)-C(9)-C(10)-C(11)	0(4)	C(17)-P(1)-C(29)-C(30)	-161.3(18)
O(5)-C(6)-C(11)-C(10)	179(2)	Pt(1)-P(1)-C(29)-C(30)	-31(2)
C(7)-C(6)-C(11)-C(10)	-3(3)	P(1)-C(29)-C(30)-P(2)	48(2)
O(5)-C(6)-C(11)-C(12)	7(3)	C(31)-P(2)-C(30)-C(29)	77.3(19)
C(7)-C(6)-C(11)-C(12)	-175(2)	C(37)-P(2)-C(30)-C(29)	-168.7(16)
C(9)-C(10)-C(11)-C(6)	2(3)	Pt(1)-P(2)-C(30)-C(29)	-45(2)

C(30)-P(2)-C(31)-C(32)	63.1(12)	C(45)-P(3)-C(39)-C(44)	25.6(11)
C(37)-P(2)-C(31)-C(32)	-59.2(13)	Pt(1)-P(3)-C(39)-C(44)	-97.7(9)
Pt(1)-P(2)-C(31)-C(32)	-178.5(7)	C(44)-C(39)-C(40)-C(41)	0.0
C(30)-P(2)-C(31)-C(36)	-118.4(12)	P(3)-C(39)-C(40)-C(41)	-179.9(5)
C(37)-P(2)-C(31)-C(36)	119.2(12)	C(39)-C(40)-C(41)-C(42)	0.0
Pt(1)-P(2)-C(31)-C(36)	-0.1(10)	C(40)-C(41)-C(42)-C(43)	0.0
C(36)-C(31)-C(32)-C(33)	0.0	C(41)-C(42)-C(43)-C(44)	0.0
P(2)-C(31)-C(32)-C(33)	178.4(11)	C(42)-C(43)-C(44)-C(39)	0.0
C(31)-C(32)-C(33)-C(34)	0.0	C(40)-C(39)-C(44)-C(43)	0.0
C(32)-C(33)-C(34)-C(35)	0.0	P(3)-C(39)-C(44)-C(43)	179.9(7)
C(33)-C(34)-C(35)-C(36)	0.0	C(38)-P(3)-C(45)-C(50)	99.9(10)
C(34)-C(35)-C(36)-C(31)	0.0	C(39)-P(3)-C(45)-C(50)	-143.5(5)
C(32)-C(31)-C(36)-C(35)	0.0	Pt(1)-P(3)-C(45)-C(50)	-13.1(5)
P(2)-C(31)-C(36)-C(35)	-178.4(11)	C(38)-P(3)-C(45)-C(46)	-65.6(12)
C(31)-P(2)-C(37)-C(38)	-81.8(19)	C(39)-P(3)-C(45)-C(46)	51.0(9)
C(30)-P(2)-C(37)-C(38)	165.3(19)	Pt(1)-P(3)-C(45)-C(46)	-178.6(6)
Pt(1)-P(2)-C(37)-C(38)	42(2)	C(50)-C(45)-C(46)-C(47)	10.3
P(2)-C(37)-C(38)-P(3)	-49(2)	P(3)-C(45)-C(46)-C(47)	174.8(6)
C(39)-P(3)-C(38)-C(37)	170.2(17)	C(45)-C(46)-C(47)-C(48)	-11.1
C(45)-P(3)-C(38)-C(37)	-80(2)	C(46)-C(47)-C(48)-C(49)	9.7
Pt(1)-P(3)-C(38)-C(37)	36(2)	C(47)-C(48)-C(49)-C(50)	-5.8
C(38)-P(3)-C(39)-C(40)	-45.0(11)	C(46)-C(45)-C(50)-C(49)	-7.0
C(45)-P(3)-C(39)-C(40)	-154.5(5)	P(3)-C(45)-C(50)-C(49)	-172.3(6)
Pt(1)-P(3)-C(39)-C(40)	82.2(5)	C(48)-C(49)-C(50)-C(45)	4.5
C(38)-P(3)-C(39)-C(44)	135.1(13)		

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[1] Commercial $MeNO_2$ contains traces of propionitrile that poisons Pt^{2+} catalysts; for purification, see: F. W. Parrett, M. S. Sun, *J. Chem. Educ.* **1977**, *54*, 448.

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