

Supporting Information for:

**Insertion of Dioxygen into a Platinum(II)–Methyl Bond To Form a Pt(II)
Methylperoxide Complex**

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Materials and Methods

General Considerations

Unless otherwise noted, all transformations were carried out under a N₂ atmosphere in a dry box (O₂ < 1 ppm) or with standard Schlenk techniques. Glassware was dried overnight in an oven prior to use. THF, toluene, and pentane were purified by passage through columns of activated alumina and molecular sieves. C₆D₆ was vacuum transferred from sodium/benzophenone ketyl. CD₂Cl₂ was vacuum transferred from CaH₂. 2-((di-*tert*-butylphosphino)methyl)pyridine (**3**) and [(μ -SEt₂)PtMe₂]₂ were synthesized using literature procedures.^{1,2} All other reagents were used as obtained from commercial suppliers. Research grade O₂ (99.999 % purity) was obtained from Airgas. NMR spectra were recorded on Bruker AV300, AV301, DRX499, and AV500 spectrometers at 298K. All coupling constants are reported in Hz. ¹H NMR spectra were referenced by using residual solvent peaks and are reported in ppm downfield of tetramethylsilane. ³¹P{¹H} NMR spectra were referenced to external H₃PO₄ (0 ppm). Multiplicity is reported as: s, singlet; d, doublet; t, triplet; br, broad; m, multiplet.

Safety Note: Caution must be taken in handling pressurized J. Young NMR tubes. Pressurized tubes were transported and stored in a protective jacket. Medium-walled J. Young NMR tubes were used for reactions with 5 atm O₂. In addition, care should be taken when handling molecular oxygen, which can liquefy at liquid N₂ temperature. Liquid oxygen is a powerful oxidant, and can lead to combustion with organic molecules.

Synthesis of (PN)PtMe₂ (**1**)

A glass reaction vessel fitted with a Teflon stopcock and a stirbar was charged with [(μ -SEt₂)PtMe₂]₂ (0.55 g, 0.88 mmol), and ligand **3** (0.41 g, 1.7 mmol). Toluene was added (20 mL), and the vessel was sealed and heated at 100 °C for 90 min in a Neslab Ex-250HT elevated temperature bath. The volatiles were removed in vacuo, leaving a yellow solid. The solid was transferred to a vial as a suspension in a small amount of toluene (*ca.* 2 mL), and it was layered with pentane and put in the freezer overnight (-35 °C). The yellow mother liquor was discarded, and the white solid was

washed twice with cold pentane and dried to yield **1** (0.69 g, 86 % yield). ^1H NMR (CD_2Cl_2 , 300 MHz): δ 9.04 (d w/ ^{195}Pt satellites, ^3H , $^3J_{\text{H-H}} = 5.5$, H_6), 7.81 (t, 1H, $^3J_{\text{H-H}} = 7.3$, H_4), 7.48 (d, 1H, $^3J_{\text{H-H}} = 7.7$, H_3), 7.13 (t, 1H, $^3J_{\text{H-H}} = 6.4$, H_5), 3.12 (d, 2H, $^2J_{\text{P-H}} = 7.9$, CH_2), 1.25 (d, 18H, $^3J_{\text{P-H}} = 12.7$, $\text{C}(\text{CH}_3)_3$), 0.84 (d w/ ^{195}Pt satellites, 3H, $^3J_{\text{P-H}} = 6.1$, $^2J_{\text{Pt-H}} = 87.3$, PtCH_3 trans to N), 0.41 (d w/ ^{195}Pt satellites, 3H, $^3J_{\text{P-H}} = 7.2$, $^2J_{\text{Pt-H}} = 64.2$, PtCH_3 trans to P). ^1H NMR (C_6D_6 , 300 MHz): δ 9.25 (d w/ ^{195}Pt satellites, ^3H , $^3J_{\text{H-H}} = 5.0$, H_6), 6.93 (t, 1H, $^3J_{\text{H-H}} = 7.4$, H_4), 6.58 (d, 1H, $^3J_{\text{H-H}} = 7.2$, H_3), 6.28 (t, 1H, $^3J_{\text{H-H}} = 5.8$, H_5), 2.53 (d, 2H, $^2J_{\text{P-H}} = 7.1$, CH_2), 1.73 (d w/ ^{195}Pt satellites, 3H, $^3J_{\text{P-H}} = 6.0$, $^2J_{\text{Pt-H}} = 88.5$, PtCH_3 trans to N), 1.43 (d w/ ^{195}Pt satellites, 3H, $^2J_{\text{P-H}} = 7.2$, $^3J_{\text{Pt-H}} = 65.4$, PtCH_3 trans to P), 1.11 (d, 18H, $^3J_{\text{P-H}} = 12.5$, $\text{C}(\text{CH}_3)_3$). ^{31}P NMR (CD_2Cl_2 , 121.5 MHz): δ 64.3 (s w/ ^{195}Pt satellites, $^1J_{\text{P-Pt}} = 1970$). ^{31}P NMR (C_6D_6 , 121.5 MHz): δ 64.6 (s w/ ^{195}Pt satellites, $^1J_{\text{P-Pt}} = 1950$). HMQC data (CD_2Cl_2 , ^1H : 500 MHz, ^{13}C : 125.7 MHz): δ 9.05, 149.3 (H_6 , C_6); 7.81, 137.0 (H_4 , C_4); 7.48, 123.6 (H_3 , C_3); 7.13, 123.1 (H_5 , C_5); 3.12, 35.2 (CH_2); 1.25, 29.1 ($\text{C}(\text{CH}_3)_3$); 0.84, -25.5 (PtCH_3 trans to N); 0.41, 13.6 (PtCH_3 trans to P). Anal. Calcd. For $\text{C}_{16}\text{H}_{30}\text{NPt}$: C, 41.55; H, 6.54; N, 3.03. Found: C, 41.64; H, 6.67; N, 2.99.

X-ray Structure of **1**

X-ray quality crystals of **1** were grown by slow evaporation of a THF solution of **1** (29.4 mg in 1 mL) at room temperature. The ORTEP of **1** is shown in figure S1.

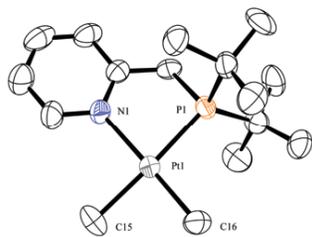


Figure S1. ORTEP diagram of **1** with ellipsoids at 50 % probability. Hydrogen atoms are excluded for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Pt1-C16} = 2.038(8)$, $\text{Pt1-C15} = 2.087(7)$, $\text{Pt1-N1} = 2.137(6)$, $\text{Pt1-P1} = 2.2743(17)$; $\text{C16-Pt1-C15} = 86.5(3)$, $\text{C15-Pt1-N1} = 92.4(3)$, $\text{N1-Pt1-P1} = 82.98(16)$, $\text{C16-Pt1-P1} = 98.5(2)$.

Synthesis of (PN)PtMe(OOMe) (2)

A J.Young NMR tube was charged with **1** (7.3 mg) and CD₂Cl₂ was added by vacuum transfer (0.48 ml, 33 mM). The tube was pressurized with 5 atm of O₂, and the tube was placed inside of a hood and allowed to react in the presence of light. After 330 minutes of reacting, species **2** and **4** were observed in a 4:1 ratio, and species **1** was not observed in the ¹H NMR spectrum. The tube was opened and the contents were poured into a vial, and X-ray crystals of **2** were grown via vapor diffusion of pentane into the CD₂Cl₂ solution at -25 °C (see figure 1 in text). NMR data for **2**: ¹H NMR (CD₂Cl₂, 500 MHz): δ 9.31 (d, 1H, ³J_{H-H} = 4.0, *H*6), 7.82 (t, 1H, ³J_{H-H} = 6.0, *H*4), 7.45 (d, 1H, ³J_{H-H} = 7.0, *H*3), 7.29 (br t, 1H, ³J_{H-H} = 6.0, *H*5), 3.75 (s, 3H, PtOOCH₃), 3.15 (d w/¹⁹⁵Pt satellites, ³ 2H, ³J_{P-H} = 9.4, CH₂), 1.30 (d, 18H, ³J_{P-H} = 13.6, C(CH₃)₃), 0.86 (s w/¹⁹⁵Pt satellites, 3H, ²J_{Pt-H} = 75.4, PtCH₃ trans to N). ¹H NMR (C₆D₆, 500 Mhz): δ 10.00 (d, 1H, ³J_{H-H} = 4.9, *H*6), 6.93 (t, 1H, ³J_{H-H} = 7.7, *H*4), 6.57 (m, 2H, *H*5+*H*3), 4.33 (s, 3H, PtOOCH₃), 2.47 (d w/¹⁹⁵Pt satellites, ³ 2H, ²J_{P-H} = 9.2, CH₂), 1.66 (s w/¹⁹⁵Pt satellites, 3H, ²J_{Pt-H} = 76.3, PtCH₃ trans to N), 1.01 (d, 18H, ³J_{P-H} = 13.5, C(CH₃)₃). ³¹P NMR (CD₂Cl₂, 202.4 MHz): 50.9 (s w/¹⁹⁵Pt satellites, ¹J_{P-Pt} = 3740). ³¹P NMR (C₆D₆, 202.4 MHz): δ 50.4 (s w/¹⁹⁵Pt satellites, ¹J_{P-Pt} = 3670). HMQC data (CD₂Cl₂, ¹H: 500 MHz, ¹³C: 125.7 MHz): δ 9.31, 147.5 (*H*₆, C₆); 7.83, 137.8 (*H*₄, C₄); 7.46, 122.8 (*H*₃, C₃); 7.29, 122.6 (*H*₅, C₅), 3.74. 64.3 (PtOOCH₃); 3.15, 34.3 (CH₂); 1.30, 28.7 (C(CH₃)₃); 0.85, -21.7 (PtCH₃).

Reaction of **1** with O₂ to form **2**

In a typical set of experiments for the reaction of **1** with O₂, a 5 ml volumetric flask was charged with **1** (55.1 mg, 0.119 mmol) and hexamethylbenzene (HMB) (2.2 mg, 0.014 mmol, internal standard) and filled with CD₂Cl₂ to make a stock solution (23.8 mM **1**, 2.7 mM HMB). The stock solution was stored in a vial in the drybox freezer (-35 °C). A syringe was used to transfer samples of 0.5 mL of the stock solution to J. Young NMR tubes. The tubes were subjected to a freeze-pump-thaw cycle on a vacuum line, and then pressurized with 5 atm O₂. The tubes were placed inside of a hood with the lights on to maintain constant light exposure. The reactions were analyzed periodically by ¹H NMR

spectroscopy, and signals were integrated against HMB (2.21 ppm in CD₂Cl₂). The reactions were complete in 7-11 h, with formation of **2** in 64-79 % yield and formation of **4** in 13-20 % yield.

Following observations that indicate a possible radical mechanism (see below), the potential reactivity of the benzyl hydrogens of the internal standard HMB was evaluated. In this control experiment, a 5 mL volumetric flask was charged with **1** (49.5 mg, 0.107 mmol), HMB (2.1 mg, 0.013 mmol), and THF (8 μ L, 0.1 mmol), and filled with CD₂Cl₂ to make a stock solution (21.4 mM **1**, 2.6 mM HMB, 20 mM THF). The stock solution was stored in a vial in the drybox freezer (-35 °C). A syringe was used to transfer samples of 0.5 mL of the stock solution to two J. Young NMR tubes. The tubes were subjected to a freeze-pump-thaw cycle on a vacuum line, and then pressurized with 5 atm O₂. The tubes were placed inside of a hood with the lights on to maintain constant light exposure. The reactions were analyzed periodically by ¹H NMR spectroscopy, and a signal for THF (1.83 ppm in CD₂Cl₂) was integrated against HMB (2.21 ppm in CD₂Cl₂) over the course of the reaction of **1** with O₂. Compared to the THF signal, the integrations of HMB were found to be constant over the course of the reaction (varying +/- by less than 3 %).

Reaction of **1 with O₂ in the Presence and Absence of Light**

Two J. Young NMR tubes were charged with 0.5 ml of a stock solution of **1** (24 mM) and HMB (2.6 mM, internal standard). The tubes were subjected to a freeze-pump-thaw cycle and pressurized with 5 atm O₂. One of the tubes (A) was kept in the presence of light and the other (B) was wrapped in foil and placed next to the first tube. The reactions were monitored over time by ¹H NMR spectroscopy. After 570 minutes, tube A contained no starting material, whereas tube B contained 42 % **1** as determined by integrations of signals in the ¹H NMR spectra of tubes A and B.

Reaction of **1 with O₂ in the presence of 4-methyl-2,6-di-*tert*-butyl-phenol (BHT)**

A J. Young tube was charged with 4-methyl-2,6-di-*tert*-butyl-phenol (BHT) (0.9 mg, 0.004 mmol). This tube and another J. Young tube were each charged with 0.5 ml of a stock solution of **1** (24 mM, 0.012 mmol) and HMB (3.0 mM, internal standard). The tubes were subjected to a freeze-pump-

thaw cycle and then pressurized with 5 atm O₂. The reactions were monitored by ¹H NMR spectroscopy. After 11 h, the tube with no BHT added contained no starting material, and a mix of species **2** (73 % yield) and **4** (13 % yield), whereas the tube with BHT contained a significant amount of **1** (ca. 71 % of the starting concentration), along with signals for species **2** (ca. 11 % yield) and **4** (ca. 11 % yield). The close proximity of the tolyl CH₃ group on BHT to the internal standard (HMB, 2.21 ppm in CD₂Cl₂) in the ¹H NMR spectrum made it difficult to obtain precise values for integrations. ¹H NMR for BHT (CD₂Cl₂, 300 MHz): 6.95 (s, 2H, ArH), 4.99 (s, 1H, OH), 2.25 (s, 3H, CH₃), 1.42 (s, 18H, C(CH₃)₃).

Synthesis of (PN)PtMe(Cl) (**4**)

A J. Young NMR tube was charged with **1** (9.5 mg, 21 mmol), and CD₂Cl₂ was added by vacuum transfer. The tube was pressurized with 5 atm O₂ and kept at room temperature in the presence of light. Species **2** was the major species after ca. 5 hr. After 5 days at room temperature, species **4** and species **2** were observed in an 85:15 ratio. Removal of the solvent under vacuum yielded a residue that was exclusively **4** as determined by NMR spectroscopy.

NMR data for **4**: ¹H NMR (CD₂Cl₂, 300 MHz): δ 9.77 (d w/¹⁹⁵Pt satellites, ³ 1H, ³J_{H-H} = 4.9, H6), 7.84 (t, 1H, ³J_{H-H} = 7.4, H4), 7.50 (d, 1H, ³J_{H-H} = 7.6, H3), 7.29 (t, 1H, ³J_{H-H} = 6.5, H5), 3.30 (d w/¹⁹⁵Pt satellites, ³ 2H, ²J_{P-H} = 10.0, CH₂), 1.32 (d, 18H, ³J_{P-H} = 14.2, C(CH₃)₃), 0.92 (s w/¹⁹⁵Pt satellites, ³ 3H, ²J_{P-H} = 70.8, PtCH₃ trans to N). ³¹P NMR (CD₂Cl₂, 121.5 MHz): δ 53.0 (s w/¹⁹⁵Pt satellites, ¹J_{P-Pt} = 4500).

X-ray Structure of **4**

X-ray quality crystals of **4** were grown via vapor diffusion of pentane into a CD₂Cl₂ solution of **4** at -25 °C. The ORTEP of **4** is shown in figure S2.

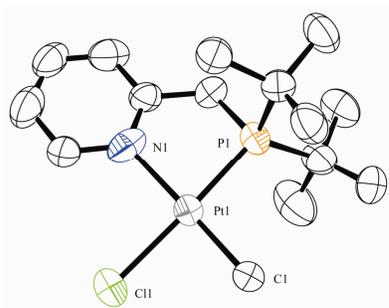


Figure S2. ORTEP diagram of **4** with ellipsoids at 50 % probability. Hydrogen atoms are excluded for clarity. Selected bond lengths (Å) and angles (°): Pt1-C1 = 2.017(11), Pt1-Cl1 = 2.368(3), Pt1-N1 = 2.111(10), Pt1-P1 = 2.205(3); C1-Pt1-Cl1 = 86.3(3), Cl1-Pt1-N1 = 92.6(3), N1-Pt1-P1 = 83.4(3), C1-Pt1-P1 = 97.9(3).

X-ray Structure Determination Details for **1**, **2**, and **4**

Table S1. Structure Determination Details for **1**, **2**, and **4**.

	1	2	4
formula	C ₁₆ H ₃₀ NPt	C ₁₆ H ₃₀ NO ₂ PPt	C ₁₅ H ₂₇ ClNPt
fw, g mol ⁻¹	462.46	494.47	482.89
temp, K	296(2)	130(2)	296(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic
space group	<i>p</i> 2 ₁ / <i>c</i>	<i>Pca</i> 2 ₁	<i>p</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.7390(18)	12.22190(15)	9.7066(8)
<i>b</i> , Å	15.252(9)	12.6523(2)	15.2493(10)
<i>c</i> , Å	15.366(3)	11.33240(15)	15.1462(15)
α, deg	90	90	90
β, deg	129.060(11)	90	128.854(4)
γ, deg	90	90	90
<i>V</i> , Å ³	1772.3(11)	1752.39(4)	1745.9(3)
<i>Z</i>	4	4	4

$D_{\text{calcd}}, \text{g cm}^{-3}$	1.733	1.874	1.837
μ, mm^{-1}	7.997	8.103	8.270
$F(000)$	904	968	936
no. of reflns for indexing	8186	3376	728
θ range for data collecn, deg	2.17 to 29.84	2.32 to 28.28	2.18 to 26.46
Index ranges	$-12 \leq h \leq 12$	$-15 \leq h \leq 15$	$-12 \leq h \leq 11$
	$-18 \leq k \leq 20$	$-16 \leq k \leq 16$	$-18 \leq k \leq 19$
	$-20 \leq l \leq 21$	$-15 \leq l \leq 15$	$-17 \leq l \leq 18$
no. of reflns collected	7976	3811	10158
no. of unique reflns (R_{int})	4502 (0.1070)	3811 (0.0000)	3461 (0.0978)
no. of data/restraints/params	4502/0/180	3811/1/199	3461/0/179
goodness of fit on F^2	S = 0.933	S = 1.169	S = 0.958
Completeness to theta, %	99.1	99.9	96.6
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0440$	$R_1 = 0.0358$	$R_1 = 0.0657$
R indices (all data)	$wR_2 = 0.1139$	$wR_2 = 0.1067$	$wR_2 = 0.1440$
Largest diff peak and hole, e \AA^{-3}	2.062 and -1.486	2.493 and -2.170	1.571 and -2.101
$w=1/[s^2*F_o^2+(aP)^2+bP]$			
a	0.0384	0.0719	0.0500
b	0	1.3057	0

Absorption correction: Semi-empirical from equivalents

Refinement method: Full-matrix least-squares on F_2

$S = \text{root}(\text{sum}(w*D*D)/(n-p))$, where $D = (F_o*F_o - F_c*F_c)$

$R_1 = \text{sum} | |F_o| - |F_c| | / \text{sum} |F_o|$

$wR_2 = \text{root}(\text{sum}(w*D*D)/\text{sum}(w*F_o*F_o))$, where $D = (F_o*F_o - F_c*F_c)$

$P = (F_o^2 + 2F_c^2)/3$

Absolute structure parameter for **2**: 0.002614(12)

Extinction coefficient for **2**: 0.0026(3)

¹ Edwards, P. G.; Fallis, I. A.; Yong, B. S. Preparation of heterocycle-containing phosphines and corresponding palladium complexes and use thereof in palladium catalyzed coupling reactions. British Patent Application GB 2378182 A, 2003.

² Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 763.

³ ¹⁹⁵Pt satellites are distinctly visible, but are broad and overlap with the central signal so that an accurate measurement of $J_{\text{Pt-H}}$ cannot be made.