Supplementary Information

for

Aerobic C–H Bond Activation at a Pd Center under Aqueous Conditions

Dae Young Bae,[a] Nicholas P. Ruhs,[b] and Liviu M. Mirica*[a]

[a] Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Avenue, Urbana, Illinois 61801, United States

[b] Department of Chemistry, Washington University in St. Louis, One Brookings Drive, St. Louis, Missouri 63130, United States

* mirica@illinois.edu

Table of Contents

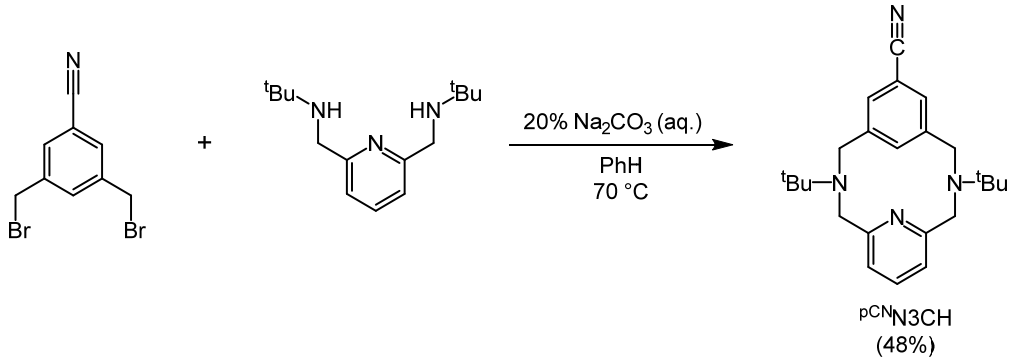
1. General Experimental Details

All operations were performed under a nitrogen atmosphere using standard Schlenk and glove box techniques if not indicated otherwise. All reagents for which the syntheses are not given were purchased from Sigma-Aldrich, Acros, STREM, or Pressure Chemical and were used as received without further purification. Solvents were purified prior to use by passing through a column of activated alumina using an MBRAUN SPS. The ligands and complex, ^{pMe}N3CH, ^{pH}N3CH, ^{pOMe}N3CH[1], N3CBr[2], and [(^{pMe}N3C)Pd^{III}(MeCN)$_2$](BF$_4$)$_2$[1] were prepared following literature procedures.

NMR spectra were obtained on a Varian Mercury-300 spectrometer (300 MHz for ^{1}H), a Varian Unity Inova-400 spectrometer (400 MHz for ^{1}H), a Varian Unity Inova-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C), or B600 Bruker NEO NMR spectrometer (600 MHz for ^{1}H, 151 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) with residual solvent resonance peaks as internal references. Abbreviations for the multiplicity of NMR signals are singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad resonance (br). EPR spectra were recorded on a Bruker 10" EMXPlus X-band Continuous Wave EPR spectrometer at 77 K. EPR spectra simulation and analysis were performed using Bruker WINEPR SimFonia program, version 1.25. UV-vis absorption spectra were recorded in 1 cm quartz cuvettes using a Varian Cary 50 Bio spectrophotometer or an Agilent Cary 60 spectrophotometer. Elemental Analysis was carried out by Intertek Pharmaceutical Services or the Microanalysis Laboratory at University of Illinois at Urbana-Champaign (UIUC) using an Exeter Analytical-Model CE440 CHN Analyzer. Cyclic voltammetry (CV) experiments were performed with a BASi EC Epsilon electrochemical workstation or a CHI 660D Electrochemical Analyzer. Electrochemical grade Bu$_4$NPF$_6$ from Fluka was used as the supported electrolyte. The electrochemical measurements were performed using a three-electrode system in a nitrogen-filled glove box. A 3 mm diameter glassy carbon disk electrode (GCE), Pt wire, and Ag wire were used as the working electrode, counter electrode, and pseudoreference electrode, respectively. The reference electrodes were calibrated against ferrocene at the end of each CV measurement. GC-MS data was collected using an Agilent 7890B GC Series System and an Agilent 5977B Mass Selective Detector. Electrospray ionization mass spectrometry (ESI-MS) was recorded on a Water Q-TOF Ultima ESI instrument by the Mass Spectrometry Laboratory at UIUC.

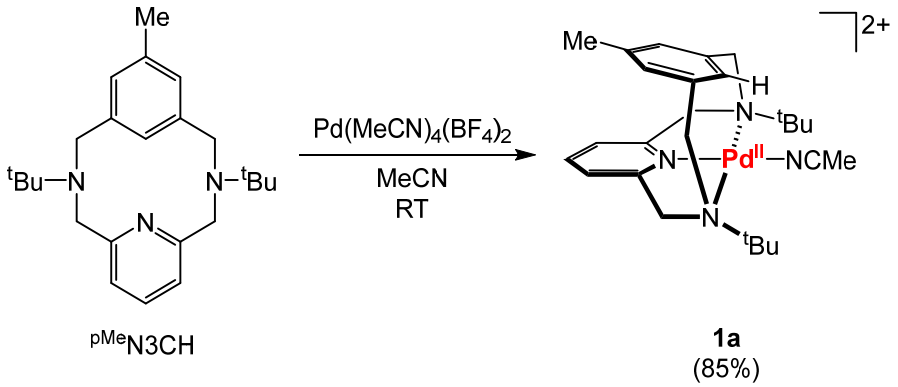
2. Synthesis of Ligands and Pd Complexes

Preparation of ^{pCN}N3CH



The ligand ^{pCN}N3CH was synthesized using a modified procedure from the literature.[1] A solution of bis[(*N*-*tert*-butylamino)methyl]pyridine (1.28 g, 5.14 mmol) in benzene (180 mL) and a 20% Na_2CO_3 aqueous solution (180 mL) was charged into a three-neck 1 L round-bottom flask equipped with an addition funnel and a magnetic stirring bar. The reaction mixture was stirred and heated to 70 °C, after which 3,5-bis(bromomethyl)benzonitrile (0.99 g, 3.43 mmol) in benzene (180 mL) was added dropwise to the reaction mixture over 1 h. The biphasic mixture was stirred at 70 °C for 2 days. Upon cooling to room temperature, the organic phase was separated. The organic layer was washed with concentrated K_2CO_3 (3 × 100 mL) and subsequently dried over $MgSO_4$. The organic layer was then filtered and evaporated to give a sticky white-yellow solid. The solid was recrystallized in methanol at -20 °C overnight. The resulting white crystalline precipitated was filtered and dried under vacuum. Yield: 624 mg (48%). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 1.31 (s, 18H, tBu–CH), 3.84 (d, *J*= 55.4 Hz, 8H, –CH_2–), 6.70 (d, *J*= 7.6 Hz, 2H), 6.98 (s, 2H), 7.13 (t, *J*= 7.6 Hz, 1H), 7.49 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 159.6, 140.8, 140.4, 135.9, 131.1, 122.6, 119.9, 110.4, 58.6, 56.0, 55.7, 27.8. Anal. Calcd. For $C_{24}H_{32}N_4$: C, 76.55; H, 8.57; N, 14.88; found: C, 76.92; H, 8.47; N, 14.66.

Preparation of [(^{pMe}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$ (1a)

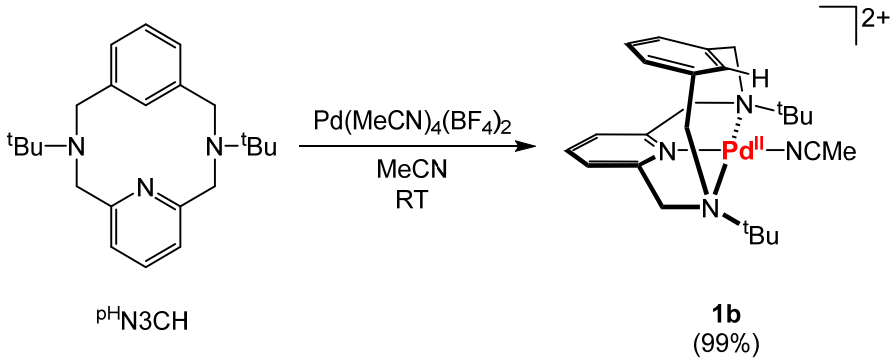


^{pMe}N3CH

1a
(85%)

To a suspension of ^{pMe}N3CH (74.7 mg, 0.204 mmol) in MeCN (2 mL) was added a solution of Pd(MeCN)$_4$(BF$_4$)$_2$ (90.8 mg, 0.204 mmol) in MeCN (1 mL). The resulting yellow solution was stirred for 15 minutes. The reaction solution was then filtered through a pad of Celite. A large excess of diethyl ether was added to the filtrate and the mixture stored at -35 ^{o}C for 1.5 hours. The product crashed out of solution as a bright yellow solid. The mixture was decanted, and the isolated product was dried under vacuum. Yield: 119.3 mg (85%). ^{1}H NMR (300 MHz, CD$_3$CN), δ: 1.52 (s, 18H, tBu–CH), 1.96 (s, 3H, NC–Me) 1.98 (s, 3H, Ph–Me), 3.70-3.85 (br, 2H, –CH$_2$–), 3.97 (m, 2H, –CH$_2$–), 4.40-4.70 (br, 4H, –CH$_2$–), 6.81 (s, 2H, Ph–H$_{meta}$), 7.00 (d, J = 7.3 Hz, 2H, Py–H$_{meta}$), 7.68 (t, J = 7.9 Hz, 1H, Py–H$_{para}$). ^{13}C NMR (125 MHz, CD$_3$COCD$_3$), δ: 164.8 151.3 141.7 140.7 140.3 138.5 138.5 138.2 136.5 134.1 133.1 118.2 68.4 67.5 57.0 56.9 55.7 25.3 21.2 20.5 4.5. Anal. Found: C, 46.11; H, 5.71; N, 8.63; calc. for C$_{26}$H$_{38}$B$_2$F$_8$N$_4$Pd: C, 45.48; H, 5.58; N, 8.16.

Preparation of [(^{pH}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$ (1b)

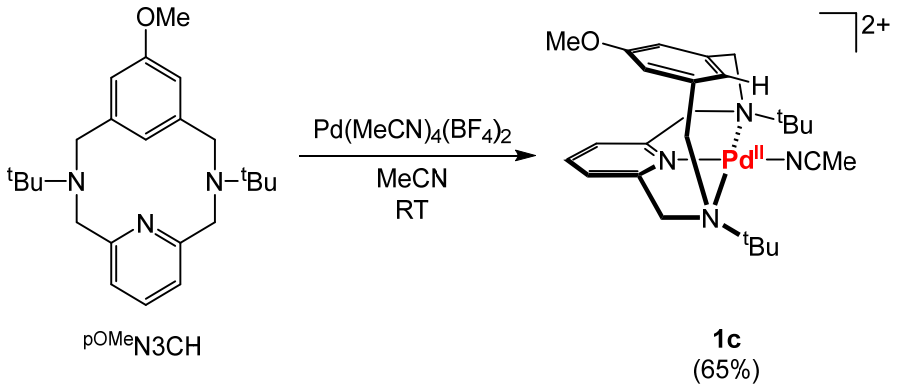


^{pH}N3CH

1b
(99%)

To a suspension of ^{pH}N3CH (39.4 mg, 0.112 mmol) in MeCN (1 mL) was added a solution of Pd(MeCN)$_4$(BF$_4$)$_2$ (49.8 mg, 0.112 mmol) in MeCN (0.75 mL). The resulting orange solution was stirred for 15 minutes. The reaction solution was then filtered through a cotton plug. A large excess of diethyl ether was added to the filtrate and the mixture stored at -35 ºC for 1.5 hours. The product crashed out of solution as a yellow/orange solid. The mixture was decanted, and the isolated product was dried under vacuum. Yield: 75.0 mg (99 %). ^{1}H NMR (300 MHz, CD$_3$CN), δ: 1.53 (s, 18H, tBu–CH), 1.97 (s, 3H), 3.80-3.95 (br, 2H, –CH$_2$–), 4.01 (m, 3H, –CH$_2$–), 4.35-4.60 (br, 3H, –CH$_2$–), 6.86 (t, *J* = 7.5 Hz, 1H, Ph–H$_{para}$), 6.97-7.04 (br, 4H, Ph–H$_{meta}$ and Py–H$_{meta}$), 7.57 (t, *J* = 7.8 Hz, 1H, Py–H$_{para}$), 9.63 (br, 1H). ^{13}C NMR (125 MHz, CD$_3$COCD$_3$), δ: 164.7, 151.0, 141.3, 139.7, 138.9, 138.2, 136.2, 133.5, 133.2, 131.5, 130.0, 118.9, 68.5, 67.3, 57.0, 56.8, 55.7, 25.3, 15.4, 4.5. Anal. Found: C, 44.44; H, 5.58; N, 8.30; calc. for C$_{25}$H$_{36}$B$_2$F$_8$N$_4$Pd: C, 44.64; H, 5.40; N, 8.33.

Preparation of [(^{pOMe}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$ (1c)

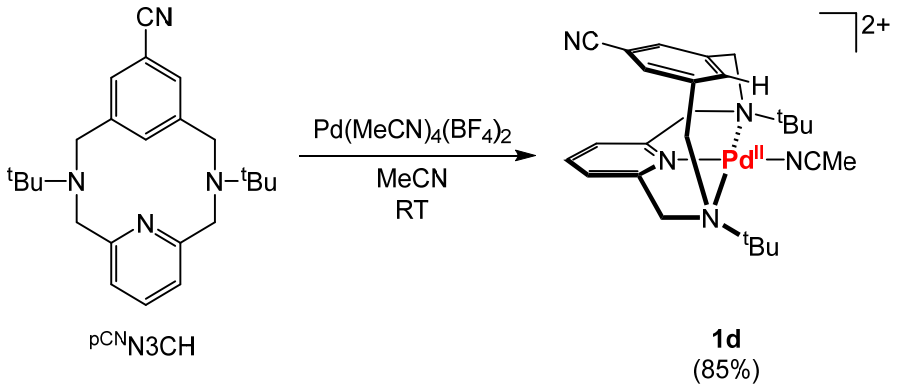


^{pOMe}N3CH

1c
(65%)

To a solution of ^{pOMe}N3CH (50.0 mg, 0.131 mmol) in MeCN (2.5 mL) was added a solution of Pd(MeCN)$_4$(BF$_4$)$_2$ (58.2 mg, 0.131 mmol in MeCN (2.5 mL). The resulting yellow solution was stirred for 15 minutes. The reaction solution was then filtered through a pad of Celite. A large excess of diethyl ether was added to the filtrate and the mixture stored at -35 ºC for 1.5 hours. The product crashed out of solution as an off-yellow solid. The mixture was decanted, and the isolated product was dried under vacuum. Yield: 76.5 mg (83%). ^{1}H NMR (500 MHz, CD$_3$SOCD$_3$), δ: 1.46 (s, 18H, tBu–CH), 2.07 (s, 3H), 3.58 (s, 3H, OMe–H), 3.63-4.40 (m, 6H, –CH$_2$–), 3.99 (d, *J*= 16.6 Hz, 2H, –CH$_2$–), 6.50 (s, 2H, Ph–H$_{meta}$), 7.02 (d, *J*= 7.5 Hz, 2H, Py–H$_{meta}$), 7.61 (t, *J*= 7.8 Hz, 1H, Py–H$_{para}$), 9.16 (s, 1H). ^{13}C NMR (151 MHz, CD$_3$SOCD$_3$), δ: 164.5, 160.0, 138.2, 136.6, 128.6, 128.6, 118.1, 117.8, 55.2, 55.2, 26.5, 24.5, 1.13. Anal. Found: C, 44.68; H, 5.64; N, 8.17; calc. for C$_{26}$H$_{38}$B$_2$F$_8$N$_4$OPd: C, 44.44; H, 5.45; N, 7.97.

Preparation of [(^{pCN}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$ (1d)

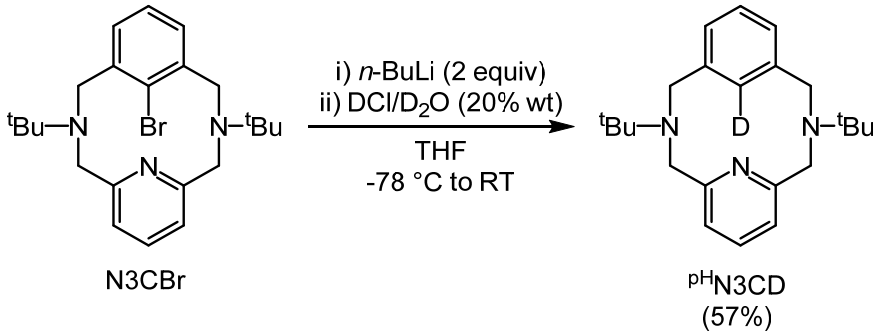


^{pCN}N3CH

1d
(85%)

To a solution of ^{pCN}N3CH (50.0 mg, 0.133 mmol) in MeCN (1 mL) was added a solution of Pd(MeCN)$_4$(BF$_4$)$_2$ (59.0 mg, 0.133 mmol) in MeCN (1 mL). The resulting yellow solution was stirred for 15 minutes. The reaction solution was then filtered through a pad of Celite. A large excess of diethyl ether was added to the filtrate and the mixture was stored at -35 ºC for 1.5 hours. The product crashed out of solution as an off-yellow solid. The mixture was decanted, and the isolated product was dried under vacuum. Yield: 79.0 mg (85%). ^{1}H NMR (500 MHz, CD$_3$CN), δ: 1.49 (br, 18H, tBu–CH), 1.96 (s, 3H), 3.82-4.54 (m, 8H), 7.10 (br, 2H), 7.36 (s, 2H), 7.68 (t, *J*= 7.8 Hz, 1H), 9.61 (s, 1H). ^{13}C NMR (151 MHz, CD$_3$CN at -20 ºC), δ: 167.1, 163.5, 141.5, 140.9, 140.4, 138.1, 135.0, 128.5, 127.5, 121.4, 121.0, 119.3, 118.3, 114.1, 72.8, 65.6, 61.7, 57.5, 57.3, 54.8, 28.7, 27.4, 24.9, 23.8. Anal. Found: C, 44.28; H, 5.09; N, 9.98; calc. for C$_{26}$H$_{35}$B$_2$F$_8$N$_5$Pd: C, 44.76; H, 5.06; N, 10.04.

Preparation of ^{pH}N3CD



The synthesis of ^{pH}N3CD ligand was modified from the literature.[2] A solution of N3CBr (100 mg, 0.232 mmol) in tetrahydrofuran (4 mL) was cooled to -78 °C. The two-equivalent amount of *n*-butyllithium (290.4 μL of 1.6 M in hexanes, 0.465 mmol, 2.0 equiv) was added dropwise to the mixture. The mixture was allowed to warm to room temperature while stirring. After reaching room temperature, the solution was stirred over 30 minutes. An excessive amount of DCl/D_2O (20 w/w%, 300 μL) was added to the mixture and the mixture stirred for an additional 10 minutes. The mixture was cooled using ice/water bath followed by the addition of saturated aqueous NaOH solution (1 mL). The organic layer was extracted with dichloromethane (3 × 1 mL). The organic layer was dried over $MgSO_4$. The organic layer was then filtered and evaporated to give white-yellow solid. The solid was washed with pentane (2 × 0.5 mL) then dried to afford white solid. The deuterium incorporation was greater than 99% which was determined by GC-MS isotope distribution or ^{1}H NMR (see Figure S1, S2, S13, and S14.). Yield: 47 mg (57%). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.17(s, 18H), 3.77 (s. 4H), 3.95 (s, 4H), 6.65 (d, *J*= 7.6 Hz, 2H), 6.81-6.94 (m, 4H).

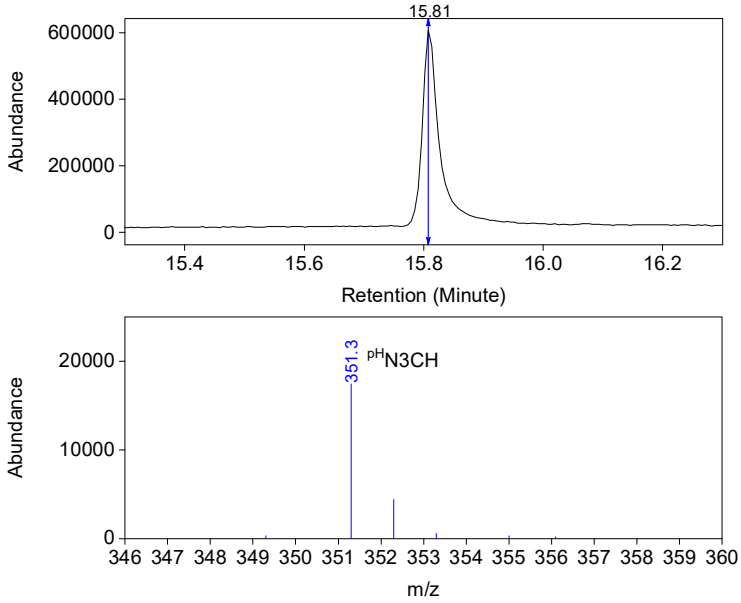


Figure S1. GC spectrum (top) and isotope distribution spectrum in MS (bottom) of ^{pH}N3CH.

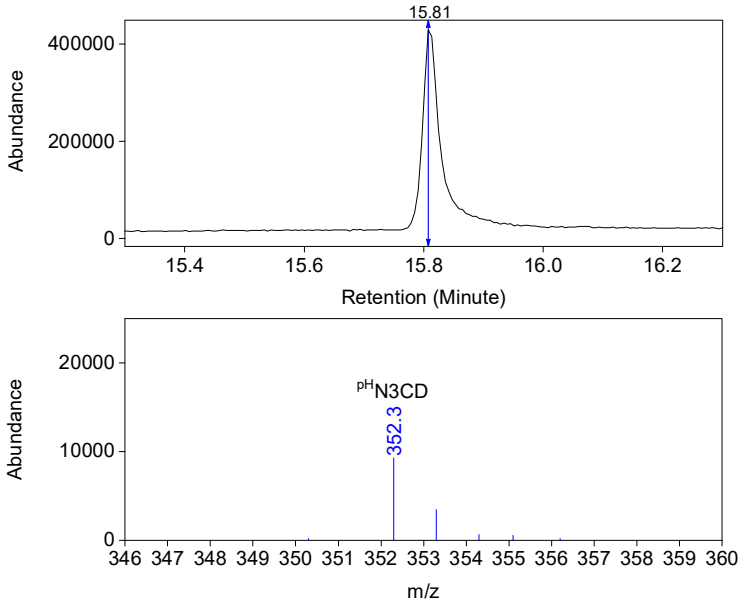


Figure S2. GC spectrum (top) and isotope distribution spectrum in MS (bottom) of ^{pH}N3CD.

3. NMR Spectral Data

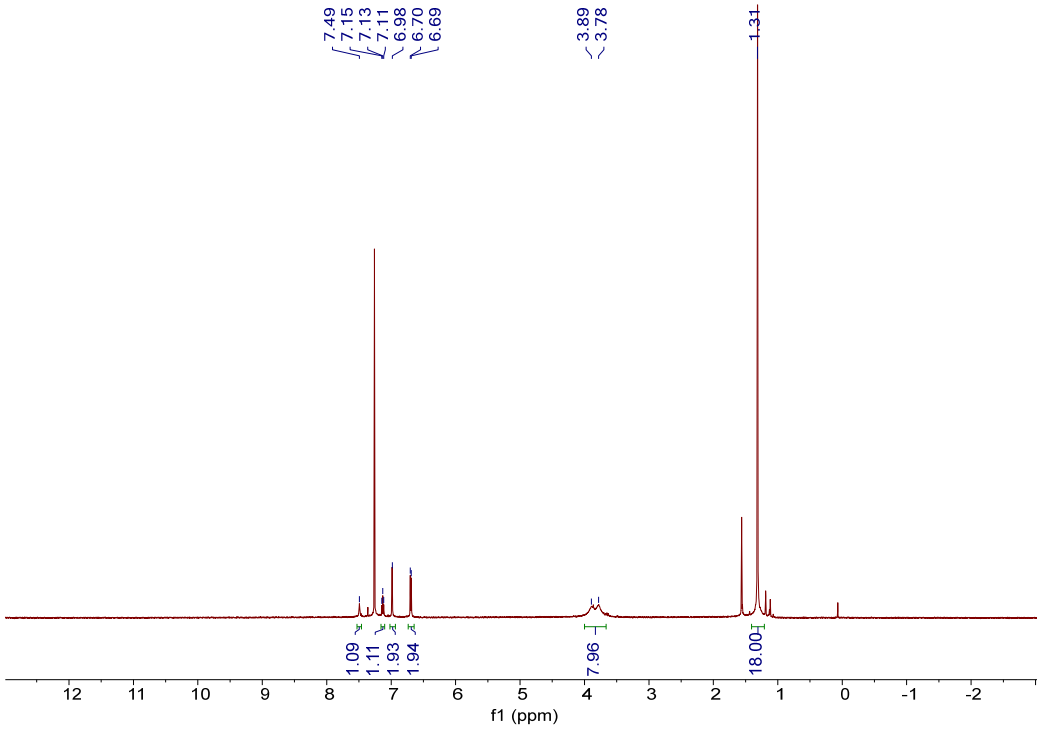


Figure S3. ^{1}H NMR spectrum of ^{pCN}N3CH at 23 °C ($CDCl_3$).

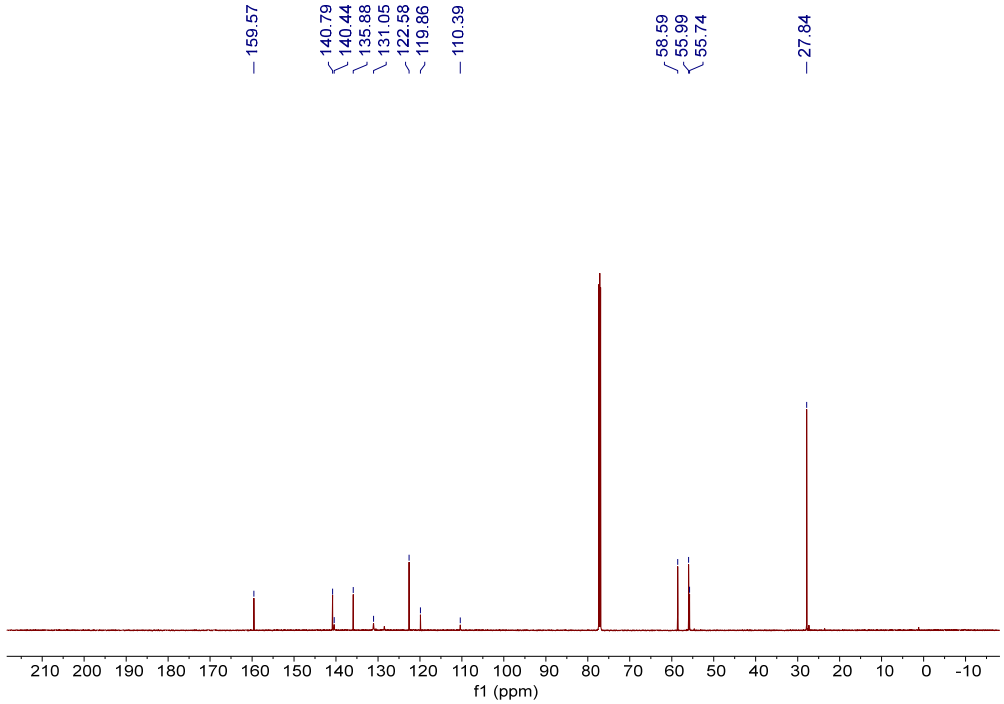


Figure S4. ^{13}C NMR spectrum of ^{pCN}N3CH at 23 °C ($CDCl_3$).

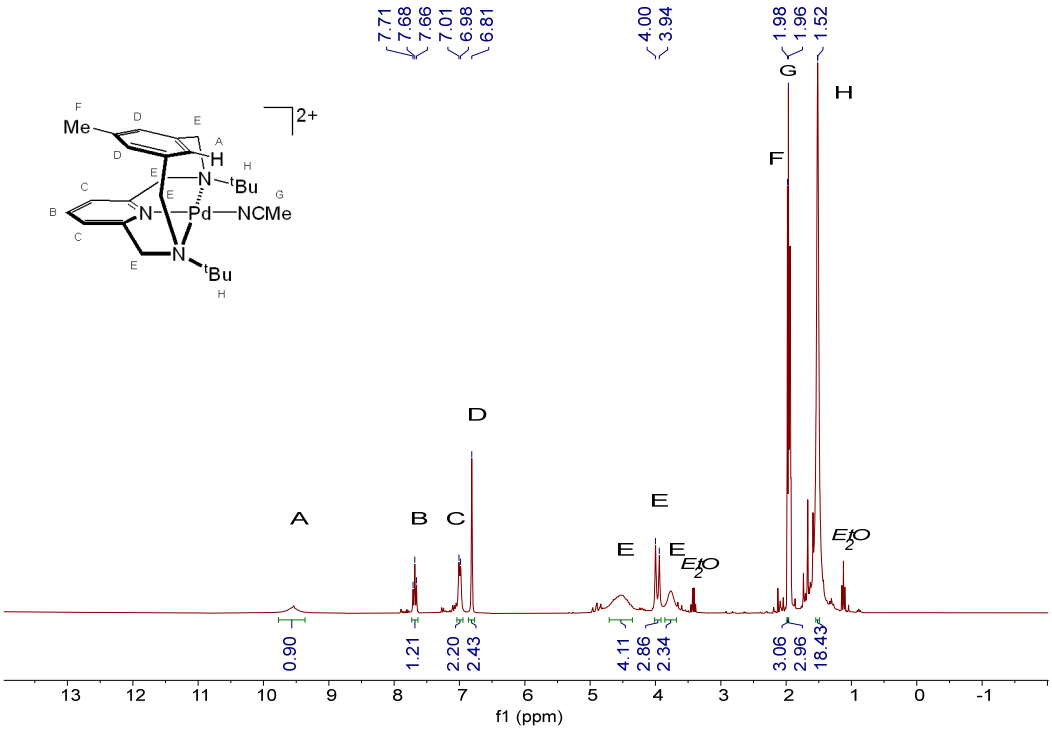


Figure S5. ^{1}H NMR spectrum of **1a** at 23 °C (CD_3CN).[a]

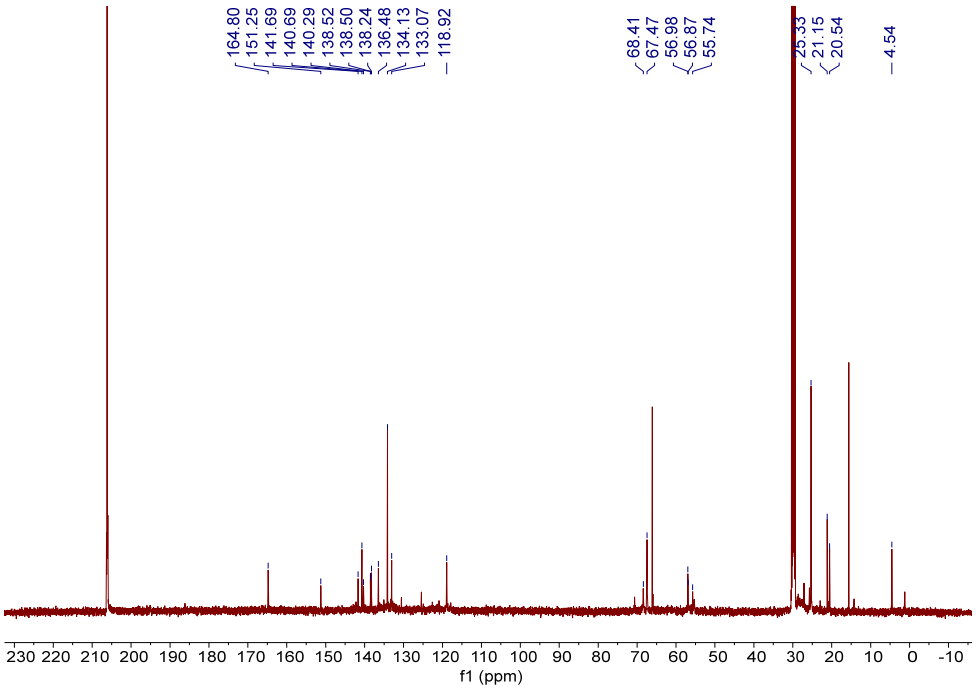


Figure S6. ^{13}C NMR spectrum of **1a** (CD_3COCD_3).

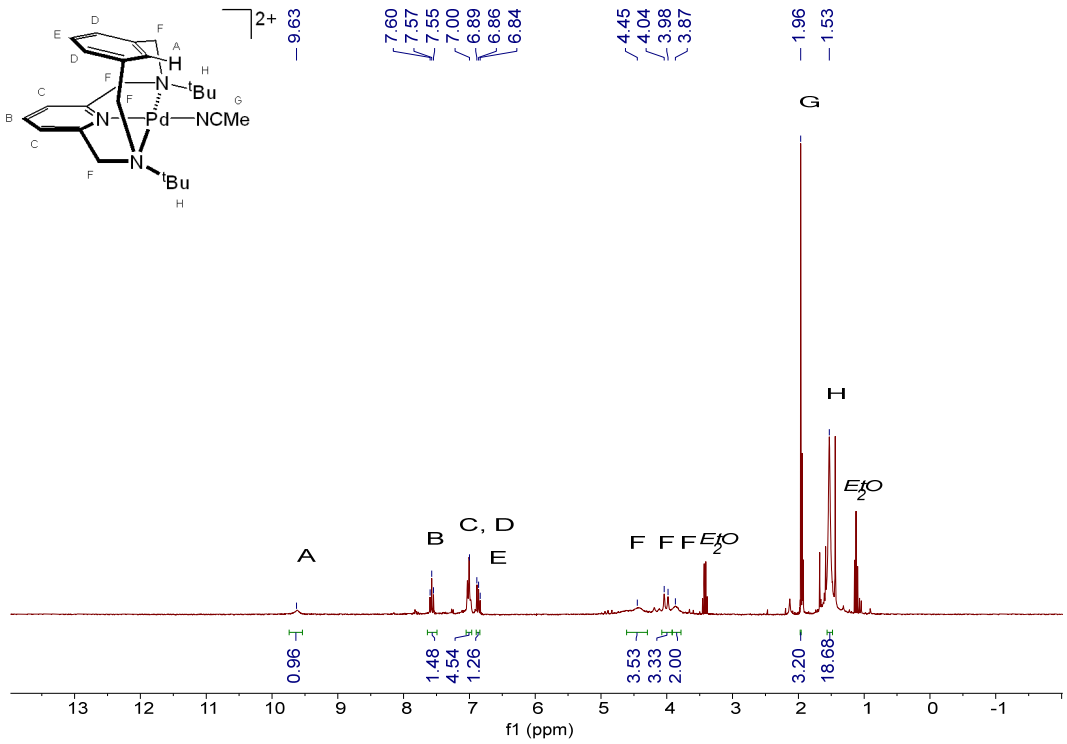


Figure S7. ^{1}H NMR spectrum of **1b** at 23 °C (CD_3CN).[a]

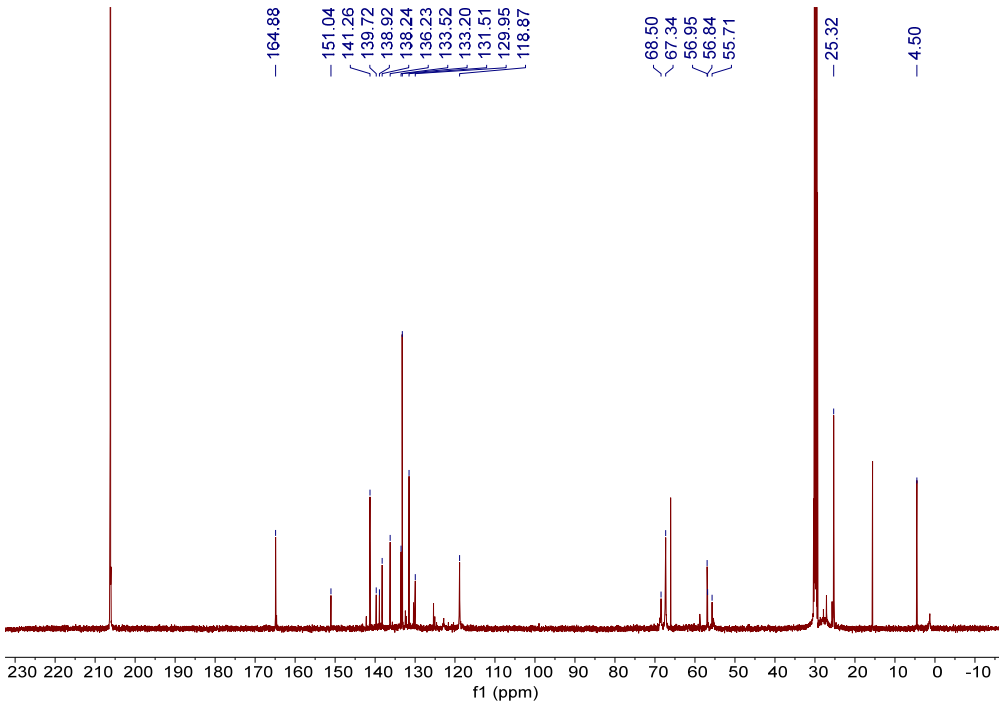


Figure S8. ^{13}C NMR spectrum of **1b** (CD_3COCD_3).

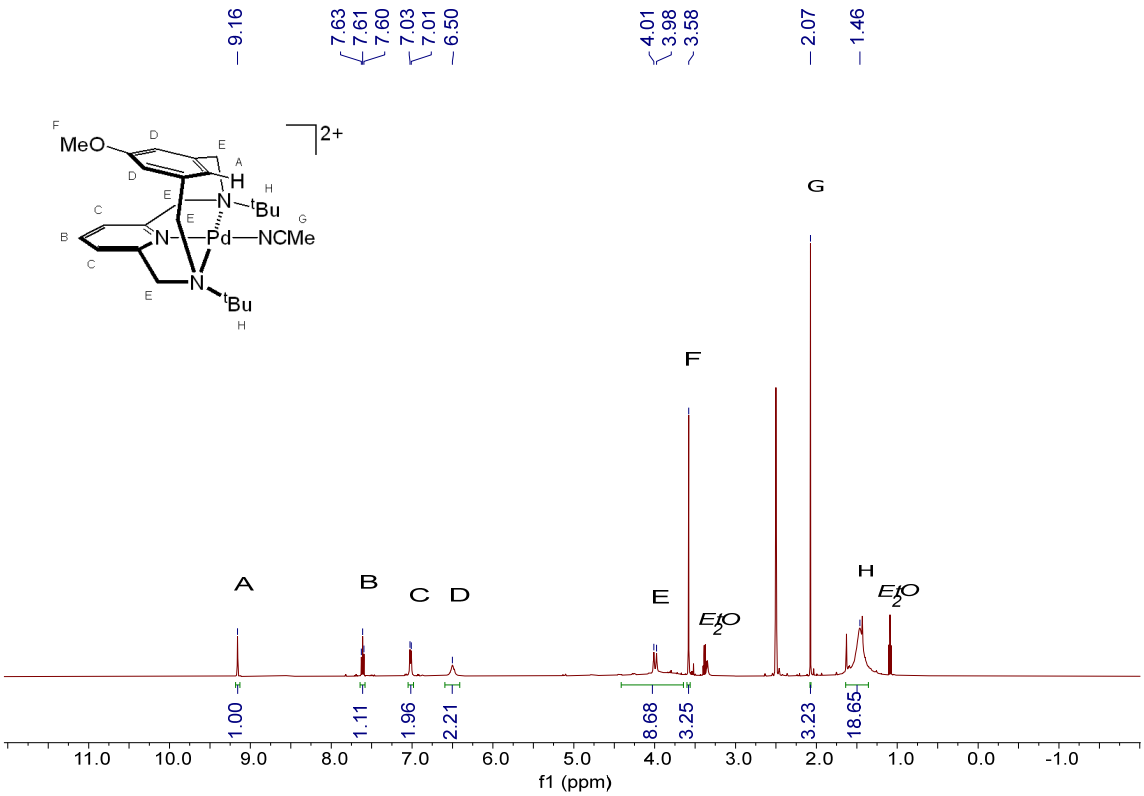


Figure S9. ^{1}H NMR spectrum of **1c** at 23 °C (CD_3SOCD_3).[a]

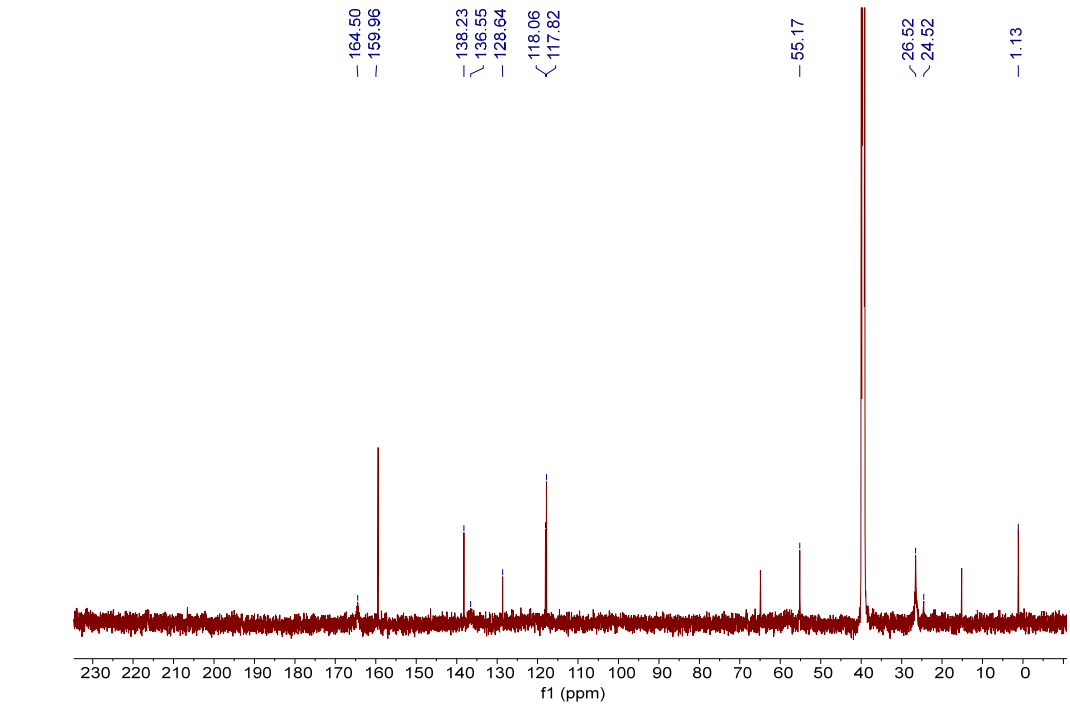


Figure S10. ^{13}C NMR spectrum of **1c** at 23 °C (CD_3SOCD_3)

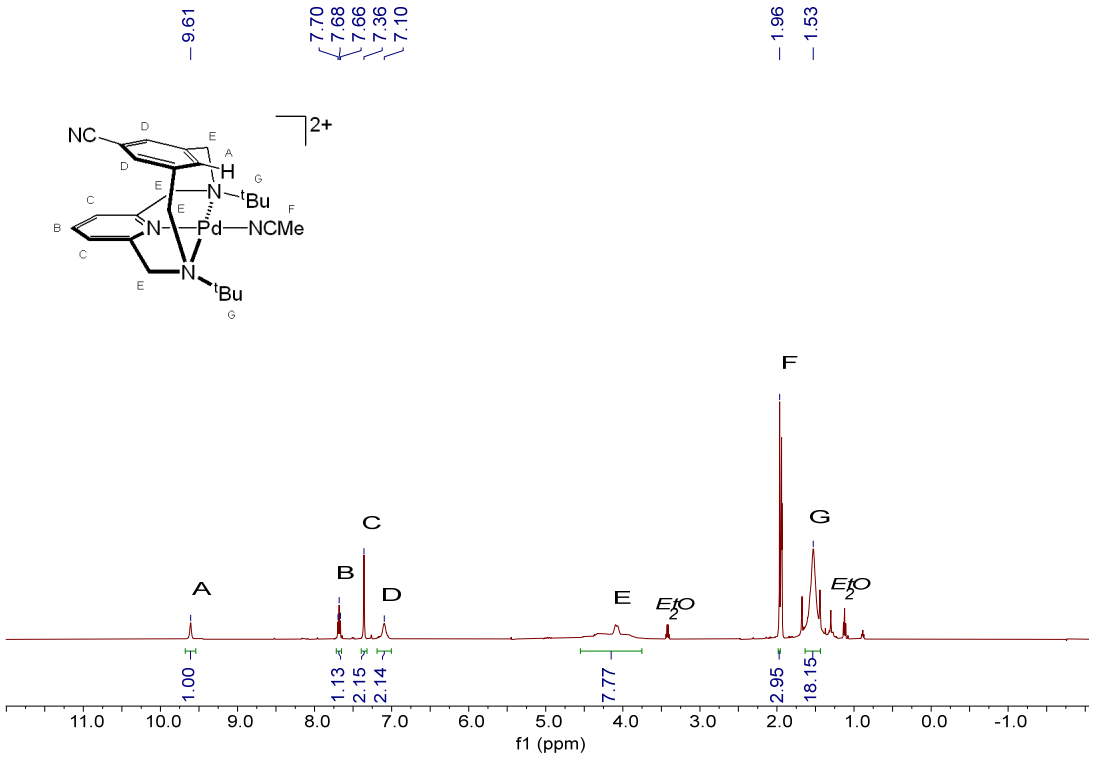


Figure S11. ^{1}H NMR spectrum of **1d** at 23 °C (CD_3CN).[a]

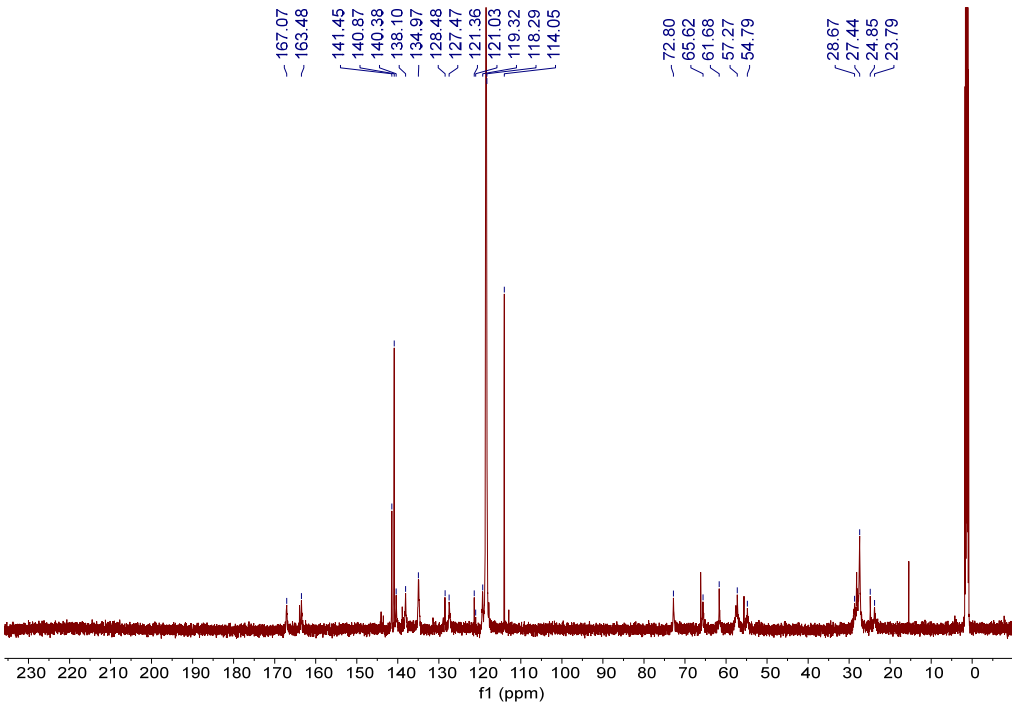


Figure S12. ^{13}C NMR spectrum of **1d** at -20 °C (CD_3CN).

[a] The additional resonances and baseline features observed in the aryl and alkyl regions of the ^{1}H NMR spectra of **1a-d** are attributed to minor, Pd^{II} coordination species, such as **1ab**, that arise from MeCN coordination/ligand exchange and/or conformational flexibility of the N3CH ligand framework. These weak features do not affect the assignment of the major diagnostic resonances of complexes **1a-d**.

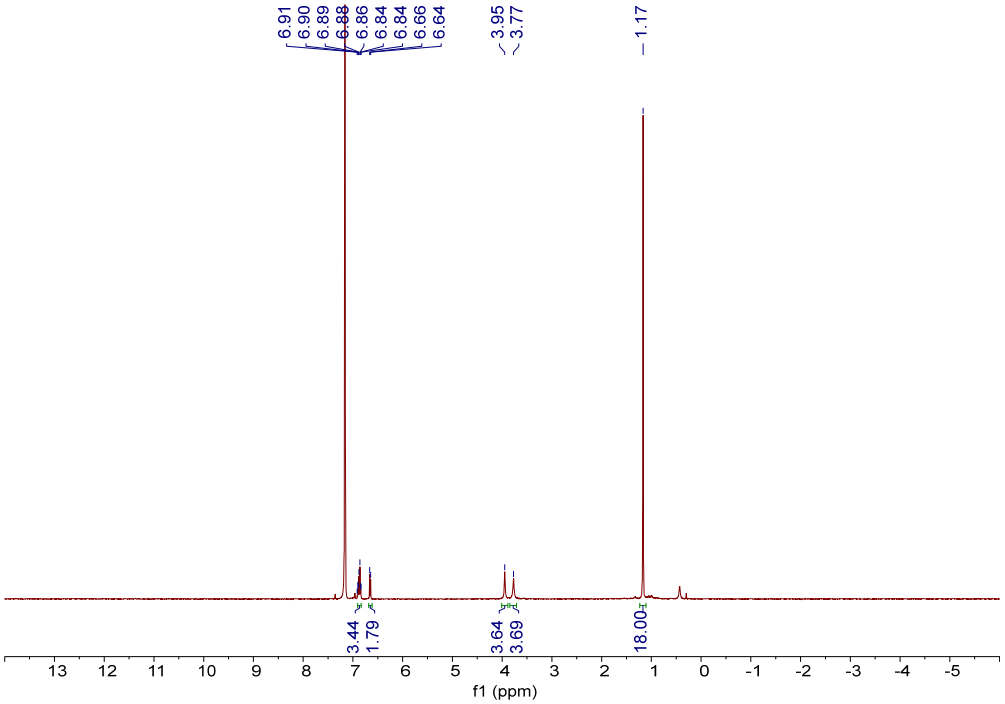


Figure S13. ^{1}H NMR spectrum of ^{pH}N3CD at 23 °C (C_6D_6).

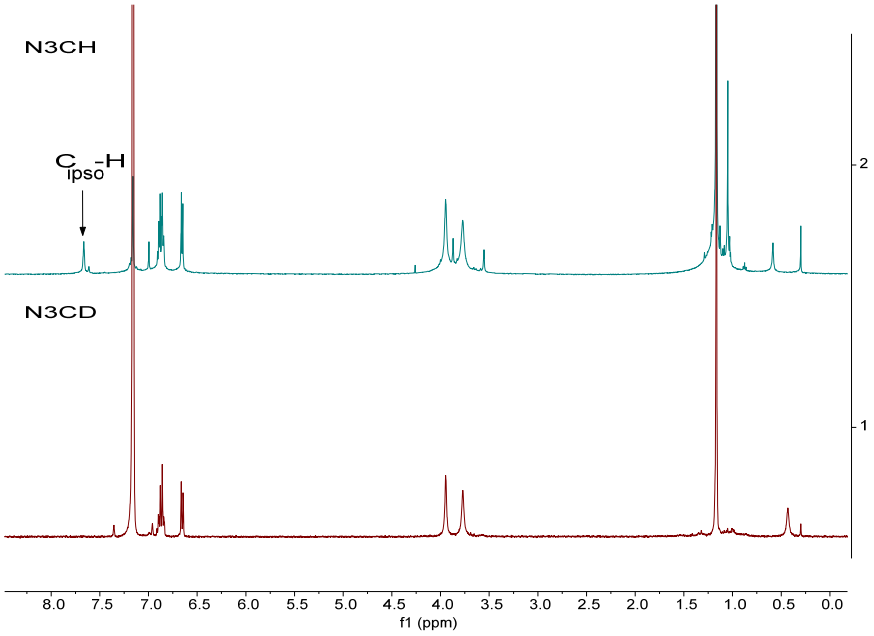


Figure S14. Comparison of ^{1}H NMR spectra of ^{pH}N3CH (top) and ^{pH}N3CD (bottom) at 23 °C (C_6D_6).

4. Electrochemical Characterization

Table S1. Summary of electrochemical data[a]

Complex	Oxidative feature (V)	Reductive feature (V)
1a	$E_{pa,ox}$ = 1.094	$E_{1/2,red}$ = -0.424
2a	$E_{1/2,ox}$ = 0.818	$E_{1/2,red}$ = -0.159

[a] Measured in 0.1 M nBu$_4$NPF$_6$ acetonitrile solution with a scan rate of 0.1 V/s. All potentials are reported relative to $Fc^{+/0}$. The irreversible oxidative feature of **1a** is reported as the anodic peak potential, $E_{pa,ox}$. Reversible or quasi-reversible waves are reported as $E_{1/2}$ values.

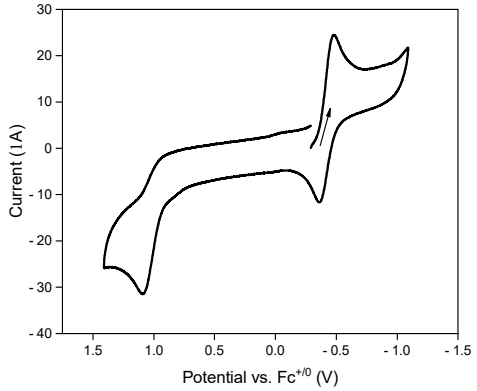


Figure S15. CV of **1a** in 0.1 M nBu$_4$NPF$_6$/MeCN (scan rate= 100 mV/s).

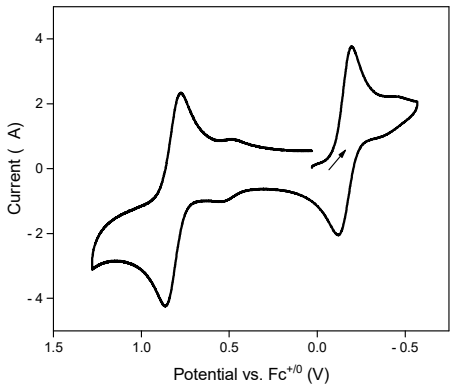


Figure S16. CV of **2a** in 0.1 M nBu$_4$NPF$_6$/MeCN (scan rate= 100 mV/s).

5. UV-Vis and Kinetic Studies of the Aerobic Oxidation of 1

a) In situ preparation of [(^{pMe}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$ (**1a**) solution

Unless specified otherwise, all solutions for Pd^{II} reactant complexes were prepared according to the procedure outlined below. To a suspension of ^{pMe}N3CH (4.6 mg, 0.0126 mmol) in MeCN (800 μL) was added a solution of Pd(MeCN)$_4$(BF$_4$)$_2$ (5.6 mg, 0.0126 mmol) in MeCN (800 μL). The resulting yellow solution was stirred at 880 rpm with a stir bar for 5 minutes to afford 7.86 mM stock solution **1a**. An aliquot (334 μL) was extracted and diluted with 2166 μL of MeCN to yield a 1.05 mM solution. Various concentrations of solutions were prepared by adjusting the volumes of aliquots from the stock solution and MeCN accordingly. For example, for 0.26 mM solution, 83 μL of stock solution, 2417 μL of MeCN; for 0.52 mM, 165 μL of stock solution, 2335 μL of MeCN; for 0.75mM, 239 μL of stock solution, 2261 μL of MeCN; for 2.1 mM, 668 μL of stock solution, 1832 μL of MeCN were used. Due to slow decomposition into palladium black, only stock solutions prepared within 30 minutes were utilized for [(^{pMe}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$. The same procedures were followed for other [(^{pR}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$ (**1b-d**) solutions.

b) Aerobic oxidation of **1** and its UV-Vis monitoring

The solution of **1** (2 mL, 0.26-2.1 mM) in MeCN was placed into a quartz cuvette (10 mm path length) equipped with a septum-sealed cap and a magnetic stir bar. To control the O_2 concentration in MeCN, gases with different oxygen/nitrogen ratio were used. The ratio of O_2/N_2 used were 100/0, 75/25, 50/50, and 20/80 to make 8.1,[3] 6.1, 4.1, and 2.4[4] mM of oxygen in MeCN. Oxygen balloons and an oxygen/nitrogen gas mixer were used to match each ratio. The balloons underwent five rounds of oxygen purging, while the mixer was flushed with gas 30 seconds prior to utilization. The inlet needle (22 G) connecting to the balloon or the purging mixer and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Each gas was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar. For the initial rate method, early time data points were obtained more than those of late and reactions that have progressed less than 5% was used for data to measure the initial rate.[5] The concentration of [(^{pR}N3CPd^{III})(MeCN)$_2$](BF$_4$)$_2$ during the reaction was calculated based on the extinction coefficient of the 550 nm absorption band (Figure S17, ε= 2128 $M^{-1}cm^{-1}$ in MeCN, 2148 $M^{-1}cm^{-1}$ in 9:1 H_2O:MeCN). The value of the extinction coefficient of the 550 nm absorption band has been updated from the previous literature[1] by

measuring thoroughly using highly purified single crystal of the complex **2a**. The same procedures were followed for other [(^{pR}N3CH)Pd^{II}(MeCN)](BF$_4$)$_2$ (**1b-d**) solutions.

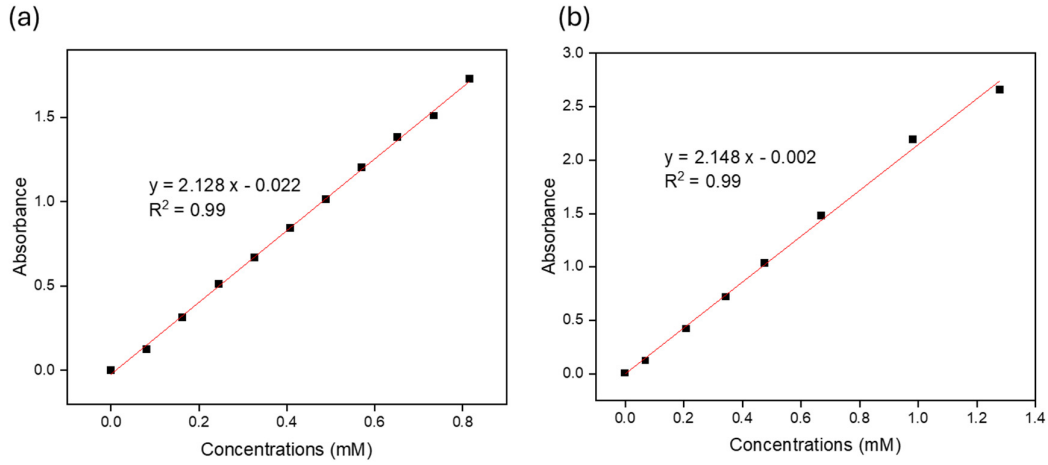


Figure S17. Beer-Lambert plots of the absorbance at 550 nm for complex **2a**. (a) MeCN (ε = 2,128 M^{-1}cm^{-1}); (b) 9:1 H_2O:MeCN (ε = 2,148 M^{-1}cm^{-1}).

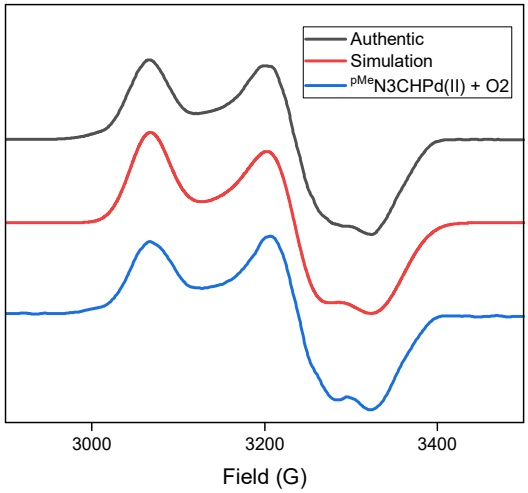


Figure S18. EPR spectrum of **2a** in 3:1 PrCN/MeCN at 77 K using the following parameters: g_x= 2.193, g_y= 2.079, g_z= 2.018 (A_z (2N)= 15.0 G). Black: isolated **2a** from the reference.[1] Red: simulated spectrum of Pd^{III}. Blue: In situ generated **2a** by the reaction mixture of **1a** with O_2.

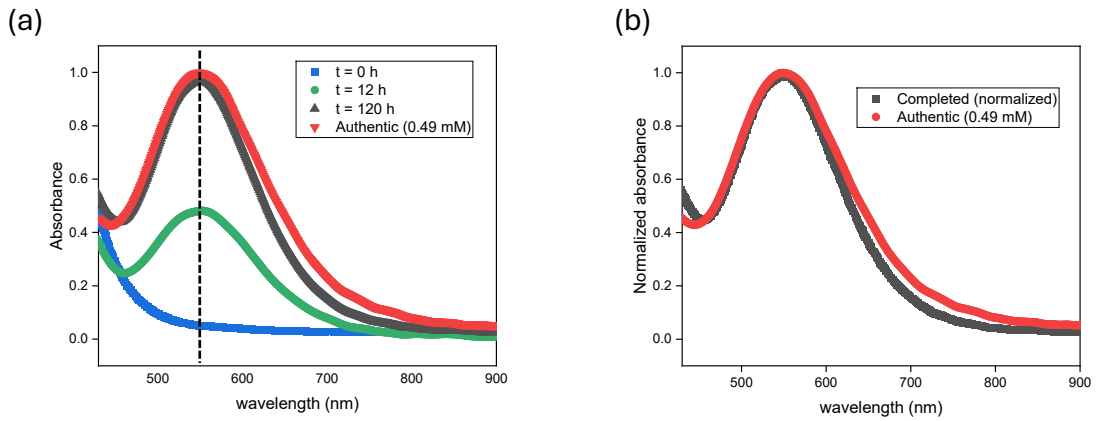


Figure S19. (a) Time-dependent UV-Vis spectra for the conversion of **1a** to **2a** in MeCN at 293 K, showing spectra at t = 0 (blue), an intermediate time point (t = 12 h, green), and at completion (t = 120 h, gray), overlaid with the spectrum of an authentic sample of **2a** (0.49 mM, red). The dashed line indicates the 550 nm wavelength. (b) Normalized overlay of the final reaction spectrum and authentic **2a** (normalized at 550 nm), highlighting the agreement in spectral shape at the monitoring wavelength.

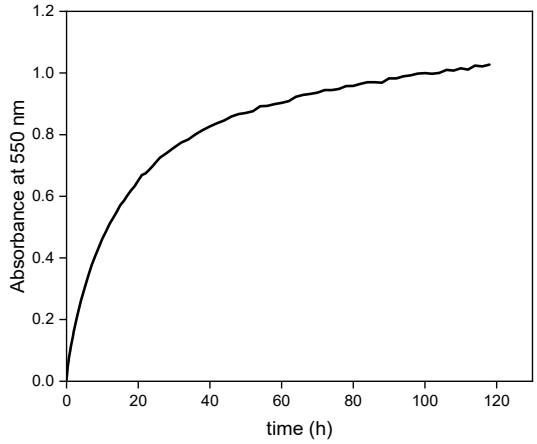


Figure S20. Absorbance (550 nm)-time graph for aerobic oxidation of **1a** at 1.05 mM O_2-saturated (8.1 mM) acetonitrile at 293 K, monitored for the entire course of the reaction.

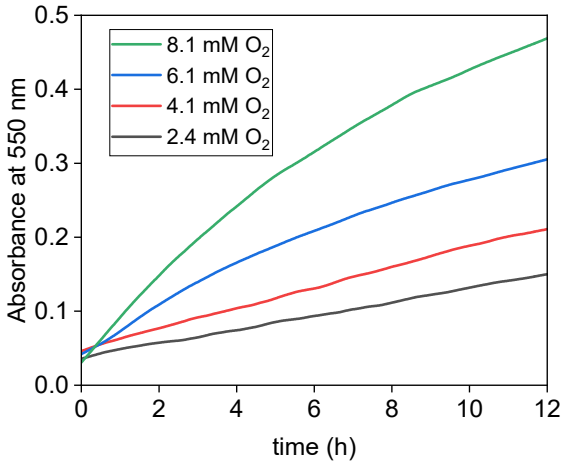


Figure S21. Absorbance (550 nm)-time graph for aerobic oxidation of **1a** (1.05 mM) with various oxygen concentrations in acetonitrile at 293 K.

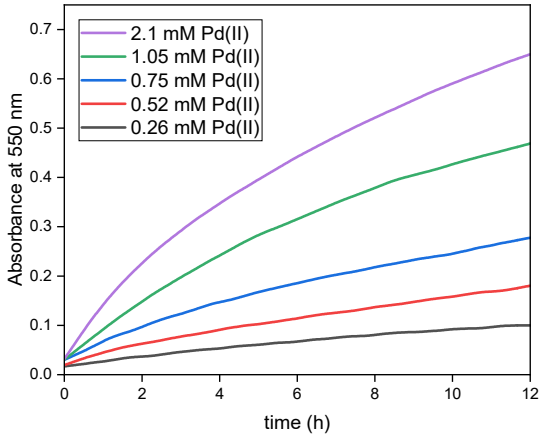


Figure S22. Absorbance (550 nm)-time graph for aerobic oxidation of **1a** at various concentrations in the O_2-saturated (8.1 mM) acetonitrile at 293 K.

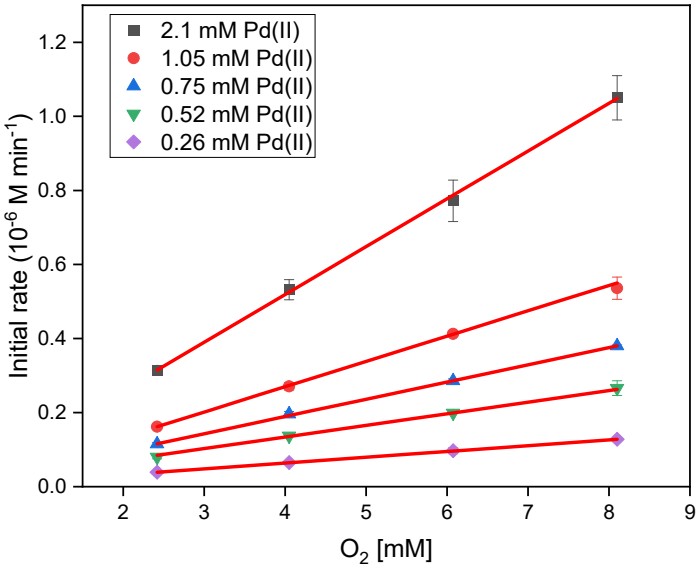


Figure S23. Plot of Initial rate vs. [O_2] of the aerobic oxidation of **1a** at 293 K. [Pd]= 0.26-2.1 mM.

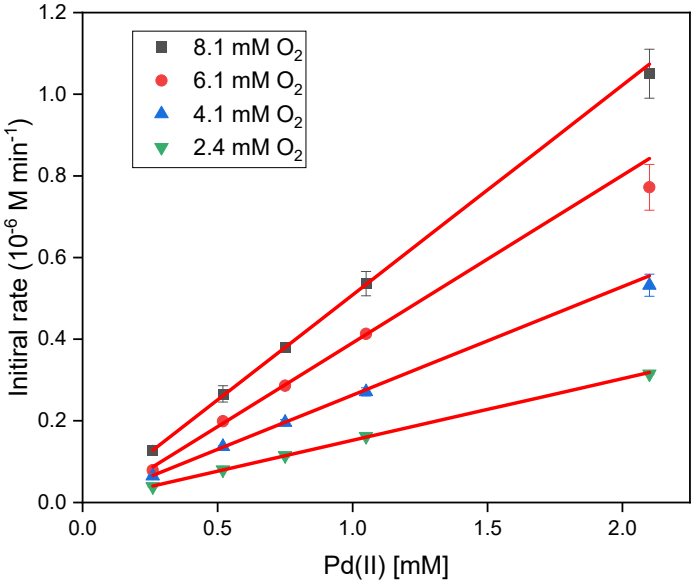


Figure S24. Plot of Initial rate vs. [Pd^{II}] of the aerobic oxidation of **1a** at 293 K. [O_2]= 2.4-8.1 mM.

Table S2. Initial rates (unit: 10^{-9} M s^{-1}) and rate constants for **1a** + O_2 at 293 K, [Pd^{II}] varied, [O_2]= 8.1 mM.

1a (mM)	O_2 (mM)	Run 1	Run 2	Run 3	Average (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})

2.1	8.1	18.0	16.5	18.2	17.5 ± 0.9	1.03 ± 0.06
1.05		8.70	9.48	8.62	8.93 ± 0.48	1.05 ± 0.06
0.75		6.30	6.38	6.32	6.33 ± 0.04	1.04 ± 0.01
0.52		4.07	4.55	4.68	4.43 ± 0.32	1.05 ± 0.01
0.26		2.15	2.13	2.13	2.14 ± 0.01	1.02 ± 0.005

Table S3. Initial rates (unit: 10^{-9} M s^{-1}) and rate constants for **1a** + O_2 at 293 K, [Pd^{II}] varied, [O_2]= 6.08 mM.

1a (mM)	O_2 (mM)	Run 1	Run 2	Run 3	Average (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})
2.1	6.08	11.8	13.7	13.1	12.9 ± 0.9	1.01 ± 0.07
1.05		6.77	6.95	6.92	6.88 ± 0.10	1.08 ± 0.02
0.75		4.82	4.68	4.83	4.78 ± 0.08	1.05 ± 0.02
0.52		3.37	3.38	3.23	3.33 ± 0.08	1.05 ± 0.03
0.26		1.77	1.53	1.53	1.61 ± 0.13	1.02 ± 0.09

Table S4. Initial rates (unit: 10^{-9} M s^{-1}) and rate constants for **1a** + O_2 at 293 K, [Pd^{II}] varied, [O_2]= 4.05 mM.

1a (mM)	O_2 (mM)	Run 1	Run 2	Run 3	Average (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})
2.1	4.05	9.07	9.18	8.37	8.87 ± 0.44	1.04 ± 0.05
1.05		4.35	4.68	4.52	4.52 ± 0.17	1.06 ± 0.04
0.75		3.15	3.38	3.25	3.26 ± 0.12	1.07 ± 0.04
0.52		2.27	2.32	2.28	2.29 ± 0.03	1.09 ± 0.01
0.26		1.05	1.05	1.12	1.07 ± 0.04	1.02 ± 0.04

Table S5. Initial rates (unit: 10^{-9} M s^{-1}) and rate constants for **1a** + O_2 at 293 K, [Pd^{II}] varied, [O_2]= 2.42 mM.

1a (mM)	O_2 (mM)	Run 1	Run 2	Run 3	Average (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})
2.1	2.42	5.22	5.30	5.23	5.25 ± 0.04	1.03 ± 0.01
1.05		2.70	2.70	2.70	2.70 ± 0.001	1.06 ± 0.001
0.75		1.87	1.98	1.90	1.92 ± 0.06	1.06 ± 0.03
0.52		1.32	1.33	1.35	1.33 ± 0.02	1.06 ± 0.01
0.26		0.63	0.65	0.65	0.64 ± 0.01	1.02 ± 0.02

Table S6. Initial rate comparison of [**1a**] and [O_2] variation at 293 K (unit: 10^{-9} M s^{-1}).

[O_2], mM	[**1a**]=2.10 mM	[**1a**]=1.05 mM	[**1a**]=0.75 mM	[**1a**]=0.52 mM	[**1a**]=0.26 mM

8.1	17.5 ± 0.9	8.93 ± 0.48	6.33 ± 0.04	4.43 ± 0.32	2.14 ± 0.01
6.08	12.9 ± 0.9	6.88 ± 0.10	4.78 ± 0.08	3.33 ± 0.08	1.61 ± 0.13
4.05	8.87 ± 0.44	4.52 ± 0.17	3.26 ± 0.12	2.29 ± 0.03	1.07 ± 0.04
2.42	5.25 ± 0.04	2.70 ± 0.001	1.92 ± 0.06	1.33 ± 0.02	0.64 ± 0.01

Table S7. Rate constant (k_{obs}) comparison of [**1a**] and [O_2] variation at 293 K (unit: 10^{-3} M^{-1} s^{-1}).

[O_2], mM	[**1a**]=2.10 mM	[**1a**]=1.05 mM	[**1a**]=0.75 mM	[**1a**]=0.52 mM	[**1a**]=0.26 mM
8.1	1.03 ± 0.06	1.05 ± 0.06	1.04 ± 0.01	1.05 ± 0.01	1.02 ± 0.005
6.08	1.01 ± 0.07	1.08 ± 0.02	1.05 ± 0.02	1.05 ± 0.03	1.02 ± 0.09
4.05	1.04 ± 0.05	1.06 ± 0.04	1.07 ± 0.04	1.09 ± 0.01	1.02 ± 0.04
2.42	1.03 ± 0.01	1.06 ± 0.001	1.06 ± 0.03	1.06 ± 0.01	1.02 ± 0.02

c) Determination of Hammett ρ Value and the Kinetic Isotope Effect (KIE)

Table S8. Initial rates (unit: 10^{-9} M s^{-1}) and rate constants of reactions of Pd^{II} + O_2.

Pd complex	Pd (mM)	O_2 (mM)	Run 1	Run 2	Run 3	Average (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})
1a	1.05	8.1	8.70	9.48	8.62	8.93 ± 0.48	1.05 ± 0.06
1b			4.60	4.88	4.90	4.79 ± 0.17	0.56 ± 0.02
1c			14.2	14.8	14.5	14.5 ± 0.3	1.71 ± 0.03
1d			0.65	0.70	0.65	0.67 ± 0.03	0.08 ± 0.003
1b-D			1.87	2.02	1.83	1.95 ± 0.08	0.23 ± 0.01

Table S9. Initial rate and rate constant comparisons for ^{pOMe}N3CH, ^{pMe}N3CH, ^{pH}N3CH, and ^{pCN}N3CH ligand systems ([Pd]= 1.05 mM, [O_2]= 8.1 mM in all experiments) at 293 K.

Ligand system	Pd	σ_{para}	Initial rate (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})
^{pOMe}N3CH	**1c**	-0.268	14.5 ± 0.3	1.71 ± 0.03
^{pMe}N3CH	**1a**	-0.17	8.93 ± 0.48	1.05 ± 0.06
^{pH}N3CH	**1b**	0.0	4.79 ± 0.17	0.56 ± 0.02
^{pCN}N3CH	**1d**	0.66	0.67 ± 0.03	0.08 ± 0.003

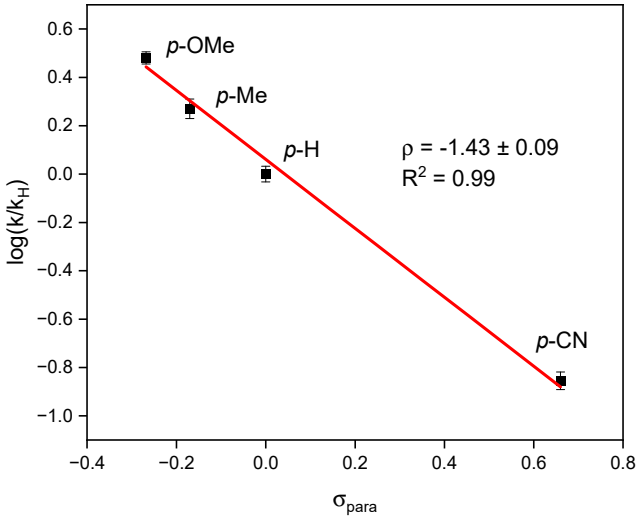


Figure S25. Hammett analysis of log(k/k_H) vs. substituent constant, σ for *para*-substituted [(^{pR}N3CH)Pd^{II}(MeCN)](BF_4)$_2$ in the aerobic C–H activation reactions at 293 K.

Table S10. Kinetic isotope effect experiments ([Pd^{II}]= 1.05 mM, [O_2]= 8.1 mM) at 293 K.

Pd	Initial rate (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})
1b	4.79 ± 0.17	0.56 ± 0.02
1b-D	1.95 ± 0.08	0.23 ± 0.01
KIE (kH/kD)	2.5 ± 0.1	2.5 ± 0.1

d) Derivation of the rate law for aerobic oxidation of **1**

$$\text{rate} = k_2[\,^3\boldsymbol{Int1}] \quad (1)$$

$$\frac{d[\,^3\boldsymbol{Int1}]}{dt} \approx 0 = k_1[\mathbf{1}][O_2] - (k_{-1}+k_2)[\,^3\boldsymbol{Int1}] \quad (2)$$

$$[\,^3\boldsymbol{Int1}] = \frac{k_1[\mathbf{1}][O_2]}{k_{-1} + k_2}$$

$$\text{rate} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{1}][O_2] \quad (3)$$

6. Aerobic Oxidation of 1 under Various Reaction Conditions

Aerobic oxidation of 1a using H_2O:MeCN (v:v) solvent mixture with various ratio

a) Aerobic oxidation of **1a** with O_2 in 1:9 H_2O:MeCN conditions

Solution of **1a** (1.17 mM) in MeCN was prepared and 1.8 mL of the solution was placed into a 4 mL quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar followed by the addition of 0.2 mL of degassed DI water to make the solution 1.05 mM. Oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar.

b) Aerobic oxidation of **1a** with O_2 in 2:8 H_2O:MeCN conditions

Solution of **1a** (1.318 mM) in MeCN was prepared and 1.6 mL of solution **1a** was placed into a 4 mL quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar followed by the addition of 0.4 mL of degassed DI water to make the solution 1.05 mM. Oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar.

c) Aerobic oxidation of **1a** with O_2 in 5:5 H_2O:MeCN conditions

Solution of **1a** (2.1 mM) in MeCN was prepared and 1.0 mL of solution **1a** was placed into a 4 mL quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar followed by the addition of 1.0 mL of degassed DI water to make the solution 1.05 mM. Oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar.

d) Aerobic oxidation of **1a** with O_2 in 9:1 H_2O:MeCN conditions

To a suspension of ^{pMe}N3CH (6.2 mg, 0.0169 mmol) in MeCN (800 µL) was added a solution of $Pd(MeCN)_4(BF_4)_2$ (7.5 mg, 0.0169 mmol) in MeCN (800 µL). The resulting yellow solution was stirred at 880 rpm with a stir bar for 5 minutes to afford 10.5 mM stock solution **1a**. An aliquot (200 µL) of the stock solution was placed into a 4 mL quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar followed by the addition of 1.8 mL of degassed DI water to make the solution 1.05 mM. Oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar.

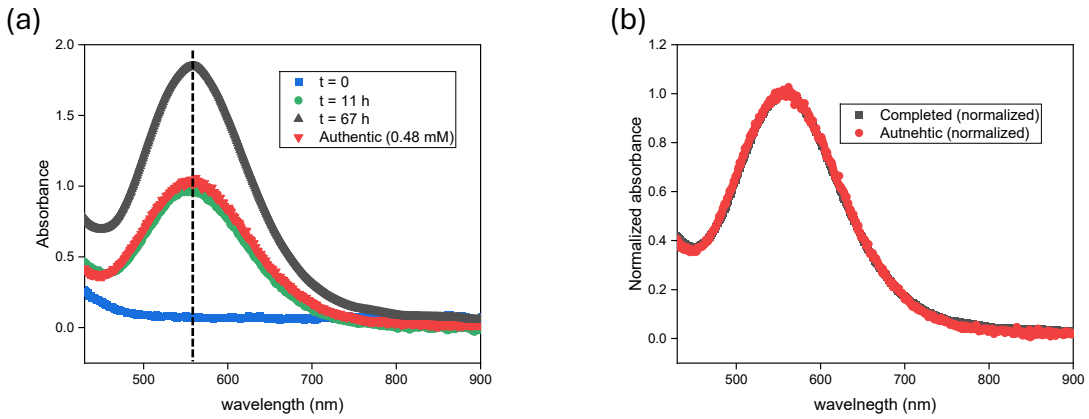


Figure S26. (a) Time-dependent UV-Vis spectra for the conversion of **1a** to **2a** in 9:1 H_2O:MeCN at 293 K, showing spectra at t = 0 (blue), an intermediate time point (t = 11 h, green), and at completion (t = 67 h, gray), overlaid with the spectrum of an authentic sample of **2a** (0.48 mM, red). The dashed line indicates the 550 nm wavelength. (b) Normalized overlay of the final reaction spectrum and authentic **2a** (normalized at 550 nm), highlighting the agreement in spectral shape at the monitoring wavelength.

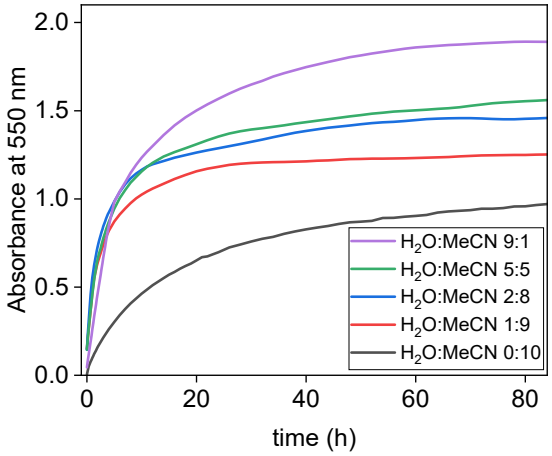


Figure S27. Absorbance (550 nm)-time graph of **1a** (1.05 mM) + O_2 in various H_2O:MeCN solvent mixture ratio.

Table S11. Yield of **2a** in various H_2O:MeCN ratio conditions. Yield was measured when the development of absorbance at 550 nm was fully completed.

H_2O:MeCN	Yield (%)
9:1	90
5:5	75
2:8	70
1:9	56
0:10	46

e) Aerobic oxidation of **1a** with O_2 in 9:1 H_2O:MeCN at different temperature

The procedure was identical to that described in part d), except that the reaction temperature was varied up to 70 °C. The concentration of O_2 in the 9:1 H_2O:MeCN solvent mixture at each temperature was estimated by a weighted average of the saturated O_2 concentrations in pure H_2O and MeCN, respectively. The solubilities of O_2 in each solvent at various temperatures were obtained from literature sources,[3, 6-8] and the solubility of O_2 in MeCN does not vary to large extent in the temperature range of interest (305.51 K to 353.13 K, 9.52 mM to 10.9 mM).[8]

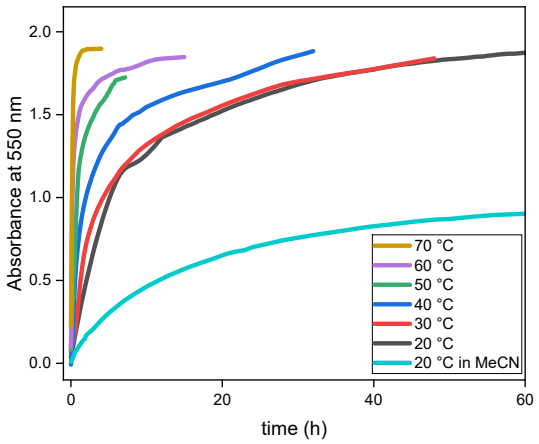


Figure S28. Time course of the 550 nm absorbance of **1a** (1.05 mM) + O_2 in 9:1 H_2O:MeCN mixture at different temperatures, and reference graph of **1a** (1.05 mM) + O_2 in MeCN (cyan).

Table S12. Yield of **2a** in 9:1 H_2O:MeCN at different temperature. Yield was measured when the development of absorbance at 550 nm was fully completed.

Temp (°C)	Reaction completion time (h)	Yield (%)
20	67	90
30	48	82
40	32	85
50	6	81
60	5	81
70	1.5	90

Table S13. Initial rate (unit: 10^{-9} M s^{-1}) and rate constant in the reaction of **1a** (1.05 mM) + O_2 in 9:1 H_2O:MeCN at different temperatures.

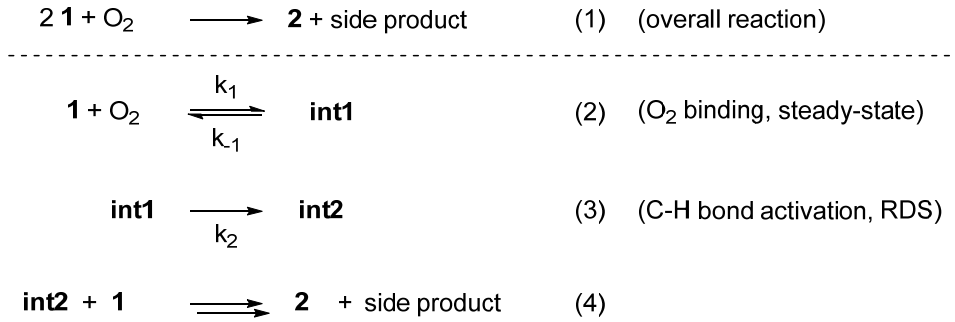
T (K)	**1a** (mM)	O_2 (mM)	Run1	Run2	Run3	Average (10^{-9} M s^{-1})	k_{obs} (10^{-3} M^{-1} s^{-1})
293	1.05	1.91	32.5	35.7	31.1	33.1 ± 2.3	16.5 ± 1.2
303		2.04	56.3	47.9	48.5	50.9 ± 4.7	23.8 ± 2.2
313		1.91	119.9	115.0	109.8	114.9 ± 5.0	57.3 ± 2.5
323		1.87	206.2	214.3	227.9	216.1 ± 11.0	110 ± 5.6
333		1.82	659.3	641.1	713.4	671.3 ± 37.6	351 ± 20
343		1.81	1469.1	1393.1	1611.8	1491.3 ± 111.1	785 ± 58

Full Time-Course Kinetic Analysis and Comparison with Initial Rate Method

To carefully evaluate the validity of the initial rate treatment, the full time-course data were analyzed by nonlinear least-squares fitting to a second-order kinetic model. The rate constants derived from the initial rate method were then compared with those obtained from the global fitting analysis.

MeCN conditions

In MeCN conditions, the reaction proceeds through the following stepwise processes:



To enable global fitting of the full time-course data, we derived the integrated rate expression for a second-order kinetic model, which was used to simulate the product concentration vs time profile. Mass balance relationships were incorporated to ensure accurate kinetic fitting.

Let A = [**1**], B = [O_2], and P = [**2**]. ([**1**] ≠ [O_2])

From the overall reaction (eq. 1), the observed rate the corresponding second-order rate constant (k_{obs}) can be expressed as follows using the steady-state approximation:

$$Observed\ rate = \frac{dP}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{1}][O_2] = k_{obs}[\mathbf{1}][O_2] = k_{obs}AB \quad (5)$$

A = A_0 – 2P, B = B_0 – P, where A_0, B_0 are initial concentrations of **1** and O_2 respectively.

$$\frac{dP}{dt} = k_{obs}[A_0 - 2P][B_0 - P] \quad (6)$$

$$\ln\left(\frac{(A_0 - 2P)B_0}{(B_0 - P)A_0}\right) = (A_0 - 2B_0)k_{obs}t \quad (7)$$

$$\text{Let } E = \exp\left((A_0 - 2B_0)k_{obs}t\right) \quad (8)$$

$$\frac{(A_0 - 2P)B_0}{(B_0 - P)A_0} = E(t) \quad (9)$$

$$P = \frac{A_0 B_0 (E - 1)}{EA_0 - 2B_0} \quad (10)$$

$$P = \frac{A_0 B_0 (\exp((A_0 - 2B_0)\, k_{obs}t) - 1)}{A_0 \exp(A_0 - 2B_0)\, k_{obs}t - 2B_0} \quad (11)$$

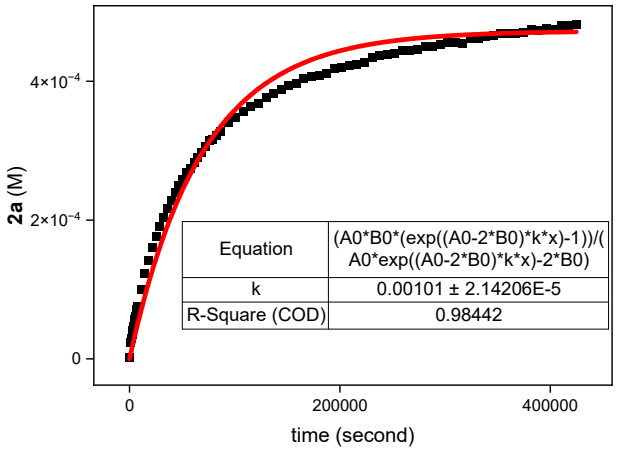


Figure S29. Nonlinear least-squares global fit of eq. 11 (red curve) to the experimental [**2a**] versus time data (black dotted) for the reaction of **1a** (1.05 mM) and O_2 (8.1 mM) in acetonitrile at 293 K. The red curve represents the simulated concentration profile obtained from the second-order kinetic model.

The integrated rate expression described above (eq. 11) was fitted to the experimental [**2**] versus time data obtained from UV-Vis spectroscopy. Nonlinear least-squares fitting afforded a global rate constant of

$$k_{\text{global}} = (1.01 \pm 0.02) \times 10^{-3}\ \text{M}^{-1}\text{s}^{-1}.$$

This value is in good agreement with the rate constant obtained from the initial rate method,

$$k_{\text{initial}} = (1.05 \pm 0.06) \times 10^{-3}\ \text{M}^{-1}\text{s}^{-1},$$

Supporting the validity of the initial rate approximation under the present experimental conditions.

Under MeCN conditions, the overall reaction (eq. 1) produces one equivalent of Pd^{III} product (**2**) per equivalent of O_2 and half equivalents of Pd^{II} (**1**) consumed. The stoichiometry-normalized rate and its rate constant in MeCN (k_{MeCN}) are expressed as follows:

$$\frac{dP}{dt} = -\frac{1}{2}\frac{dA}{dt} = -\frac{dB}{dt} = k_{MeCN}[\mathbf{1}][O_2] = k_{MeCN}AB \quad (12)$$

From eq. 5 and eq. 12, the stoichiometry-normalized rate constant (k_{MeCN}) is identical to the observed rate constant under these MeCN conditions.

9:1 H_2O:MeCN mixture conditions

Under 9:1 H_2O:MeCN conditions, the reaction proceeds according to the following overall process:

$$2\,\mathbf{1} + O_2 \longrightarrow 2\,\mathbf{2} + H_2O_2 \qquad (1) \quad \text{(overall reaction)}$$

To enable global fitting of the full time-course data, we derived the integrated rate expression for a second-order kinetic model (eq. 7), which was used to simulate the product concentration versus time profile. Mass balance relationships were incorporated to ensure accurate kinetic fitting.

Let A = [**1**], B = [O_2], and P = [**2**]. ([**1**] ≠ [O_2])

$$A = A_0 - P,\ B = B_0 - 0.5P$$

From the overall reaction (eq. 1), the observed rate and experimentally observed second-order rate constant (k_{obs}) can be expressed as follows using the steady-state approximation:

$$Observed\ rate = \frac{dP}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{1}][O_2] = k_{obs}[\mathbf{1}][O_2] = k_{obs}AB \quad (2)$$

$$= k(A_0 - P)(B_0 - \frac{1}{2}P) \quad (3)$$

$$\frac{1}{(A_0 - P)(B_0 - \frac{1}{2P})}dp = k_{obs}dt \quad (4)$$

$$ln\frac{\left(B_0 - \frac{1}{2}P\right)A_0}{(A_0 - P)B_0} = k_{obs}\left(B_0 - \frac{A_0}{2}\right)t \quad (5)$$

$$\frac{\left(B_0 - \frac{1}{2}P\right)A_0}{(A_0 - P)B_0} = \exp\left(k_{obs}\left(B_0 - \frac{A_0}{2}\right)t\right) = E(t) \quad (6)$$

$$P = \frac{2A_0B_0(E-1)}{2B_0E - A_0} \quad (7)$$

The integrated rate expression (eq. 7) was fitted to the experimental [**2**] versus time data obtained from UV-Vis spectroscopy using nonlinear least-squares analysis. The rate constants obtained from global fitting (k_{global}) were compared with those determined independently from the initial rate method ($k_{initial}$) at each reaction temperature (Table S14). The two sets of values are in good agreement, supporting the validity of the initial rate approximation under the present experimental conditions.

Under aqueous conditions (9:1 H_2O:MeCN), the overall reaction (eq. 1) produces two equivalents of Pd^{III} (**2**) per one equivalent of O_2 and two equivalents of Pd^{II} (**1**) consumed by the proposed mechanism. The stoichiometry-normalized rate and its rate constant in 9:1 H_2O:MeCN mixture conditions (k_{H2O}) are expressed as follows:

$$\frac{1}{2}\frac{dP}{dt} = -\frac{1}{2}\frac{dA}{dt} = -\frac{dB}{dt} = k_{H2O}[\mathbf{1}][O_2] = k_{H2O}AB \quad (8)$$

From eq. 2 and eq. 8, the stoichiometry-normalized reaction rate constant (k_{H2O}) is half of the observed rate constant under these 9:1 H_2O:MeCN conditions

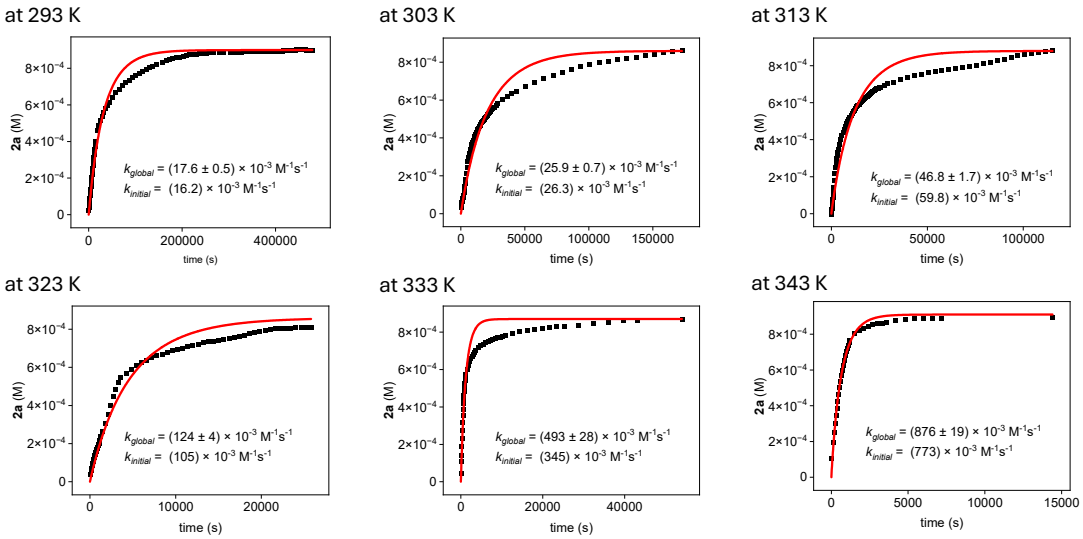


Figure S30. Global nonlinear fits of the full time-course data for formation of **2a** under 9:1 H_2O:MeCN conditions at 293–343 K (six temperatures). Experimental data (black dotted) are fit to eq. 7 (red solid). Insets list the corresponding k_{global} and $k_{initial}$ values at each temperature.

Table S14. Comparison of observed rate constants obtained from initial rate method, second-order global kinetic fitting, and normalized rate constant (k_{H2O}) at various reaction temperatures in the reaction of **1a** (1.05 mM) + O_2 under 9:1 H_2O:MeCN conditions.

Temp (K)	$k_{initial}$ (10^{-3} M^{-1} s^{-1})	k_{global} (10^{-3} M^{-1} s^{-1})	k_{H2O} (10^{-3} M^{-1} s^{-1})
293	16.5 ± 1.2	17.6 ± 0.5	8.8 ± 0.3
303	23.8 ± 2.2	25.9 ± 0.7	13.0 ± 0.4
313	57.3 ± 2.5	46.8 ± 1.7	23.4 ± 0.9
323	110 ± 5.6	124 ± 4	62.0 ± 2
333	351 ± 20	493 ± 28	247 ± 14
343	773 ± 58	876 ± 19	438 ± 10

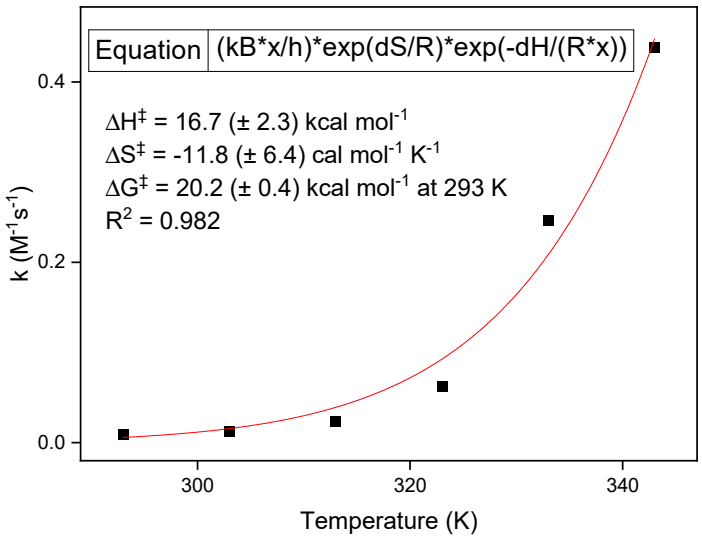


Figure S31. Nonlinear regression Eyring plot of rate constant versus temperature to determine activation parameters for the aerobic oxidation of **1a** in 9:1 H_2O:MeCN.

Stoichiometric O_2 study

Solution of **1a** (7.84 mM) in MeCN was prepared and 265 µL of solution **1a** was placed into a 4 mL quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar. Additionally, 135 µL of acetonitrile and 3.6 mL of degassed deionized water to make 0.52 mM of 4.0 mL solution to reduce the headspace as much as possible. A gas tight syringe was prepared to inject the exact amount of molecular oxygen into the cuvette. The syringe was purged 5 times with molecular oxygen before measuring the amount of oxygen. Oxygen was measured exactly depending on each equivalent (for 1 equiv: 0.0125 mmol, 302 µL; for 1/2 equiv: 0.00627 mmol, 151 µL; for 1/4 equiv: 0.00314 mmol, 75 µL). The oxygen containing syringe was inserted into the cuvette and the tip of the needle placed bottom of the cuvette with care. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar.

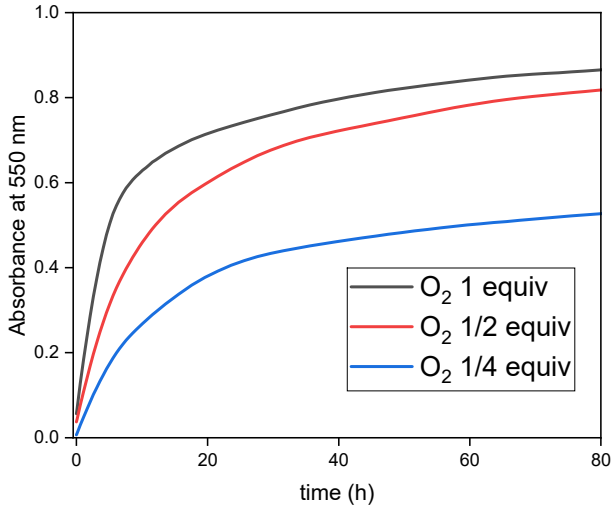


Figure S32. Absorbance (550 nm)-time graph of stoichiometric (1, 1/2, and 1/4 equiv) study of O_2 with **1a** (0.52 mM) in 9:1 H_2O:MeCN solvent mixture at 293 K.

Quantification of Hydrogen Peroxide

a) Calibration curve

The yield of the hydrogen peroxide was spectroscopically determined from the absorption at 407 nm by the Ti^{IV} oxysulfate method.[9-11]. The calibration curve for the measurement of H_2O_2 was derived the following procedure. The 10 μL of 30 wt% H_2O_2 solution was added to a 10 mL volumetric flask followed by H_2O addition to make 10 mL stock solution. The known amount of volume of the stock solution were added to each 10 mL volumetric flask followed by the addition of 0.1 mL of a 15 wt% $Ti(O)(SO_4)$ solution in H_2SO_4 and H_2O to make 10 mL of 0 mM, 0.098 mM, 0.196 mM, 0.489 mM, 0.98 mM, and 1.96 mM solutions. After mixing each solution for 5 minutes, the absorptions at 407 nm of each solution were measured to make the calibration curve (Figure S33).

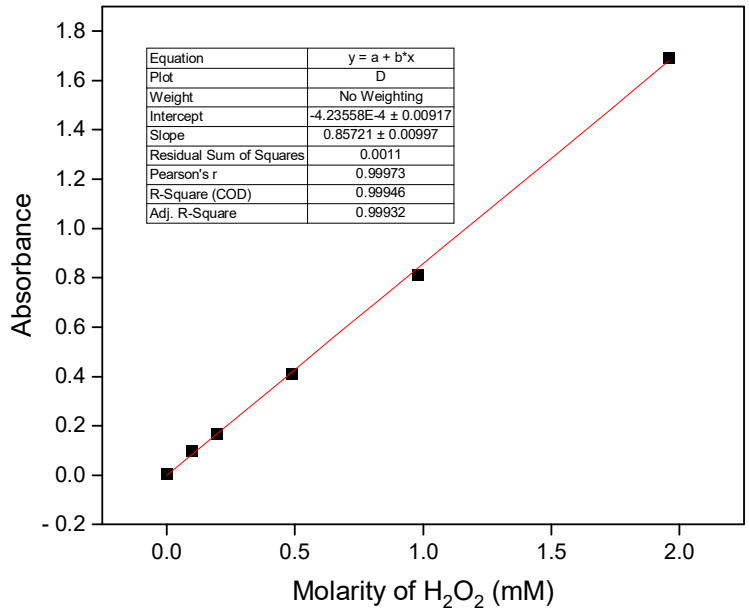


Figure S33. Calibration curve of the concentrations of H_2O_2 in aqueous solution with $Ti(O)(SO_4)$.

b) Sample preparation

A reaction was run in the same way as the section 5 in Supporting Information. When the reaction reaches 90% of the yield of Pd^{III} complex **2a** by UV-Vis spectroscopy, a 1 mL of the solution was taken. Then, to the 1 mL of the solution, 0.1 mL of a 15 wt% $Ti(O)(SO_4)$ solution in H_2SO_4 and H_2O was introduced to make the total volume of the solution to 10 mL. The absorption at 407 nm of the solution was measured and subtracted the absorbance effect from (diluted) **2a** to quantify H_2O_2 precisely, because product **2a** was highly soluble in aqueous phase which makes organic solvent extraction unable to separate H_2O_2 from **2a**. For example,

a 1.05 mM reaction solution **A** that reaches 90% yield of **2a** showed 1.05 absorbance value at 407 nm. The 1 mL of the solution **A** was taken and 0.1 mL of a 15 wt% Ti(O)(SO_4) solution and H_2O was introduced to **A** to make the 10 mL of the solution **B**. The absorption at 407 nm of solution **B** was measured as 0.145. Since the reaction solution **A** has diluted ten times in solution **B**, so the absorption without effect of **2a** will be (0.145 - 1.05/10 =) 0.04, which corresponds to 0.0467 mM of TiO_2 in solution **B**. The TiO_2 concentration in **B** can be considered as (0.0467 × 10 =) 0.467 mM of H_2O_2 in solution **A** and the yield of H_2O_2 in solution **A** is (0.467 mM /1.05 mM × 100 =) 44%. We also prepared the mock sample to investigate whether the complex in the reaction solution hinders the titanium oxysulfate method to quantify H_2O_2. The average yield of H_2O_2 in 3 trials was 42 ± 3%.

A solution of independently synthesized **2a** (0.95 mM) in 9:1 H_2O:MeCN solvent mixture and TiO_2 (0.45 mM) solution was also prepared, separately. The 1 mL of each solution and 90 μL of 15 wt% Ti(O)(SO_4) solution were added to a 10 mL volumetric flask followed by the addition of water to make 10 mL mock solution. The mock solution was measured and compared with the solution **B**. There was little difference in UV-Vis spectrum between solution **B** and the mock solution, so we conducted this method to quantify H_2O_2.

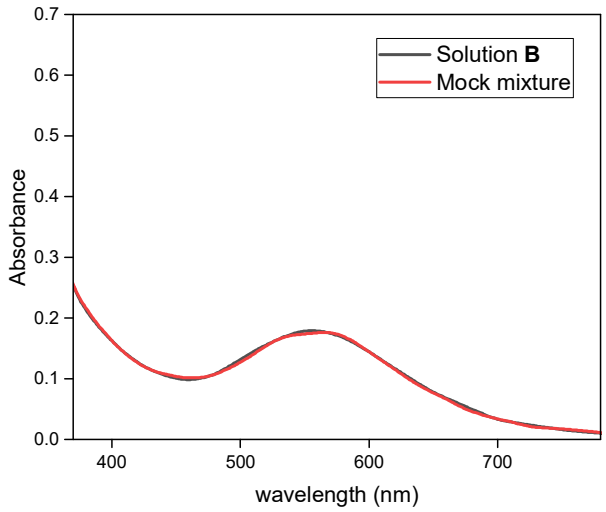


Figure S34. UV-Vis spectrum comparison of the solution **B** and mock solution: a mixture of **2a** (0.095 mM), TiO_2 (0.045 mM), and 90 μL of 15 wt% Ti(O)(SO_4) solution.

Reaction with *p*-toluenesulfonic acid

The addition of 1 equiv *p*-toluenesulfonic (tosic) acid did not result in the development of the absorbance band at 550 nm, indicating no progress to afford complex **2a** (Figure S35). An attempt to add 0.5 equiv of tosic acid after the complete development of the absorbance band at 550 nm under standard conditions was conducted, but no further growth of the band was observed (Figure S36). Additionally, when tosic acid was introduced to independently synthesized **2a**, it led to a decrease in absorbance, suggesting the decomposition of **2a** (Figure S37). These results indicate that the presence of a strong acid suppresses the reaction and does not facilitate a higher yield of **2a**.

a) Aerobic oxidation of **1a** with O_2 in the presence of *p*-toluenesulfonic acid

4.05 mL solution of **1a** (1.08 mM) in MeCN was placed into a 20 mL vial. *p*-toluenesulfonic acid monohydrate (8.3 mg, 0.0437 mmol) was weighed into a 4 mL vial then 1 mL of MeCN was added to make a solution. 100 μL of *p*-toluenesulfonic acid solution was poured into solution of **1a** to make 1.05 mM of solution **1a** in the presence of 1 equivalent of the acid. 2 mL of mixed solution was transferred into a quartz cuvette (10 mm path length) equipped with a septum-sealed cap and a magnetic stir bar. An oxygen balloon was prepared with an inlet needle, oxygen was then bubbled through the solution for 45 seconds, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm.

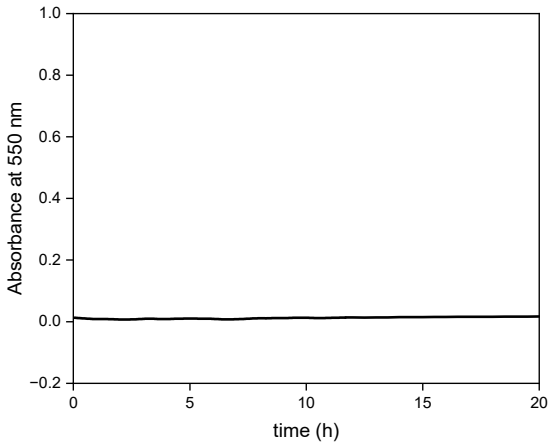


Figure S35. Absorbance (550 nm)-time graph for aerobic oxidation of **1a** with 1 equivalent of tosic acid in the O_2-saturated (8.1 mM) acetonitrile.

b) Aerobic oxidation of **1a** with O_2 then addition of *p*-toluenesulfonic acid after the complete development of the absorbance band at 550 nm under standard reaction conditions

2 mL solution of **1a** (1.05 mM) in MeCN was placed into a quartz cuvette (10 mm path length) equipped with a septum-sealed cap and a magnetic stir bar. Oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. The oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar. The development of 550 nm band was almost completed at 72 hours, 1 mL of 0.105 M tosic acid solution in MeCN was prepared. 10 μL of the acidic solution (0.5 equiv to **1a**, 0.00105 mmol) was inserted into the cuvette solution through a syringe.

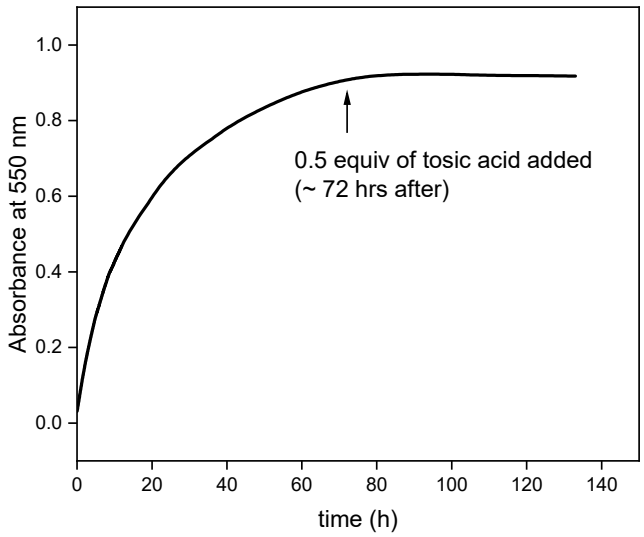


Figure S36. Absorbance (550 nm)-time graph for aerobic oxidation of **1a** in the O_2 saturated (8.1 mM) acetonitrile followed by the addition of 0.5 equiv of tosic acid when the development of absorbance at 550 nm was fully completed.

c) Stability test of **2a** in the presence of *p*-toluenesulfonic acid

The solution of independently synthesized complex **2a** in acetonitrile (2 mL, 0.178 mM) was prepared and was placed into a quartz cuvette (10 mm path length) equipped with a septum-sealed cap and a magnetic stir bar. *p*-toluenesulfonic acid monohydrate (6.7 mg, 0.0355 mmol) was weighed then dissolved by 1 mL of MeCN to obtain a solution. 10 μL of the acid solution was injected into the cuvette and the reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar.

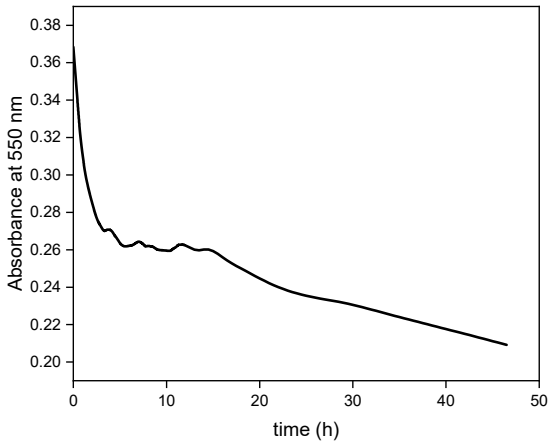


Figure S37. Absorbance (550 nm)-time graph of stability test for **2a** (0.177 mM) in the presence of *p*-toluenesulfonic acid (1 equivalent) in MeCN.

Reaction in phosphate buffered solution

We investigated the influence of a phosphate buffer[12] on reaction kinetics, expecting that the yield would increase. Surprisingly, this addition did not lead to any observable progress in the reaction (Figure S38). This suggests a potential interaction between the phosphate species and the metal complex that may impede the C–H bond activation process.

Solution of **1a** (1.17 mM) in MeCN was prepared and 1.8 mL of the solution was placed into a quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar, followed by the addition of 200 µL 0.1 M phosphate buffer solution (pH 7.4). Oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar.

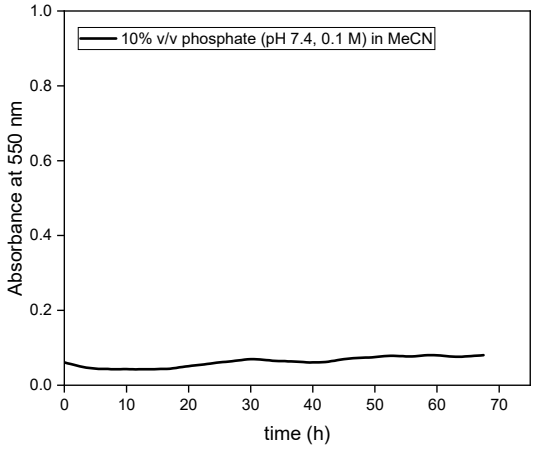


Figure S38. Absorbance (550 nm)-time graph of **1a** (1.05 mM) + O_2 in 10% v/v phosphate (pH 7.4, 0.1 M) in MeCN.

7. ESI-MS Analysis of Aerobic Oxidation of 1

Electrospray ionization mass spectrometry (ESI-MS) was employed as a qualitative probe to compare the solution-state speciation of Pd complexes generated during aerobic oxidation of **1** under MeCN or H_2O:MeCN solvent conditions. In MeCN, a signal assigned to a Pd–OH containing species was detected (Figures S40, S43, S45). In contrast, no corresponding Pd–OH signal was observed when the reaction was conducted in a 9:1 H_2O:MeCN mixture (Figure S42). The appearance of a Pd–OH species under neat MeCN conditions may arise from decomposition of an oxygenated Pd intermediate generated following the initial C–H bond activation step. One possible interpretation is that, in the absence of water, this oxygenated intermediate does not undergo subsequent C–H bond activation and instead undergoes decomposition prior to detection by ESI-MS. Notably, the absence of Pd–OH signals under aqueous conditions is consistent with the enhanced formation of the C–H activated Pd^{III} product and hydrogen peroxide, as observed experimentally in H_2O-containing solvent mixtures.

a) Aerobic oxidation of **1a** in MeCN

A solution of **1a** (1.05 mM) in MeCN (2.0 mL) was placed in a 4 mL quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar. An oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. The reaction progress was monitored by UV-Vis spectroscopy while stirring at 170 rpm with a stir bar. Several aliquots were taken during the reaction proceeds to analyze ESI-MS. At early reaction times (0–2 h), no signal corresponding to a Pd–OH containing species (m/z = 570.2419) was detected. At longer reaction times (≥26 h), a peak at m/z 570.2419 (calcd for $[(^{pMe}N3CH)Pd(OH)(MeCN)_2]^+$, 570.2424) gradually emerged and increased in intensity, becoming clearly observable after 50 h. This signal disappeared following the addition of degassed DI water (2.0 mL) to the reaction mixture, without a concomitant increase in the yield of **2a**. The appearance of the Pd–OH assigned signal under neat MeCN conditions is consistent with formation and subsequent decomposition of an oxygenated Pd species generated during the reaction. In addition, ESI-MS spectra exhibited peaks at m/z 366.2898, 310.2274, and 254.1637, corresponding to ligand-derived fragment ions, as well as peaks at 470.1788, 414.1151, and 358.0498 assignable to

[(^{pMe}N3C)Pd]$^{+}$ and its related fragment ions. A peak at m/z 235.0900 was assigned to the double charged charged species [(^{pMe}N3C)Pd]$^{2+}$.

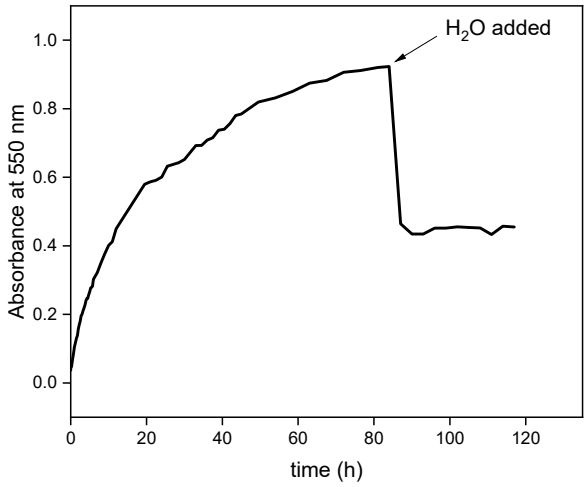


Figure S39. Time course for the 550 nm absorbance during aerobic oxidation of **1a** in O_2-saturated MeCN (8.1 mM), followed by the addition of 2 mL of water when the development of absorbance at 550 nm was fully completed. The total concentration of palladium complexes was halved (1.05 mM → 0.52 mM) upon addition of water to 2 mL MeCN.

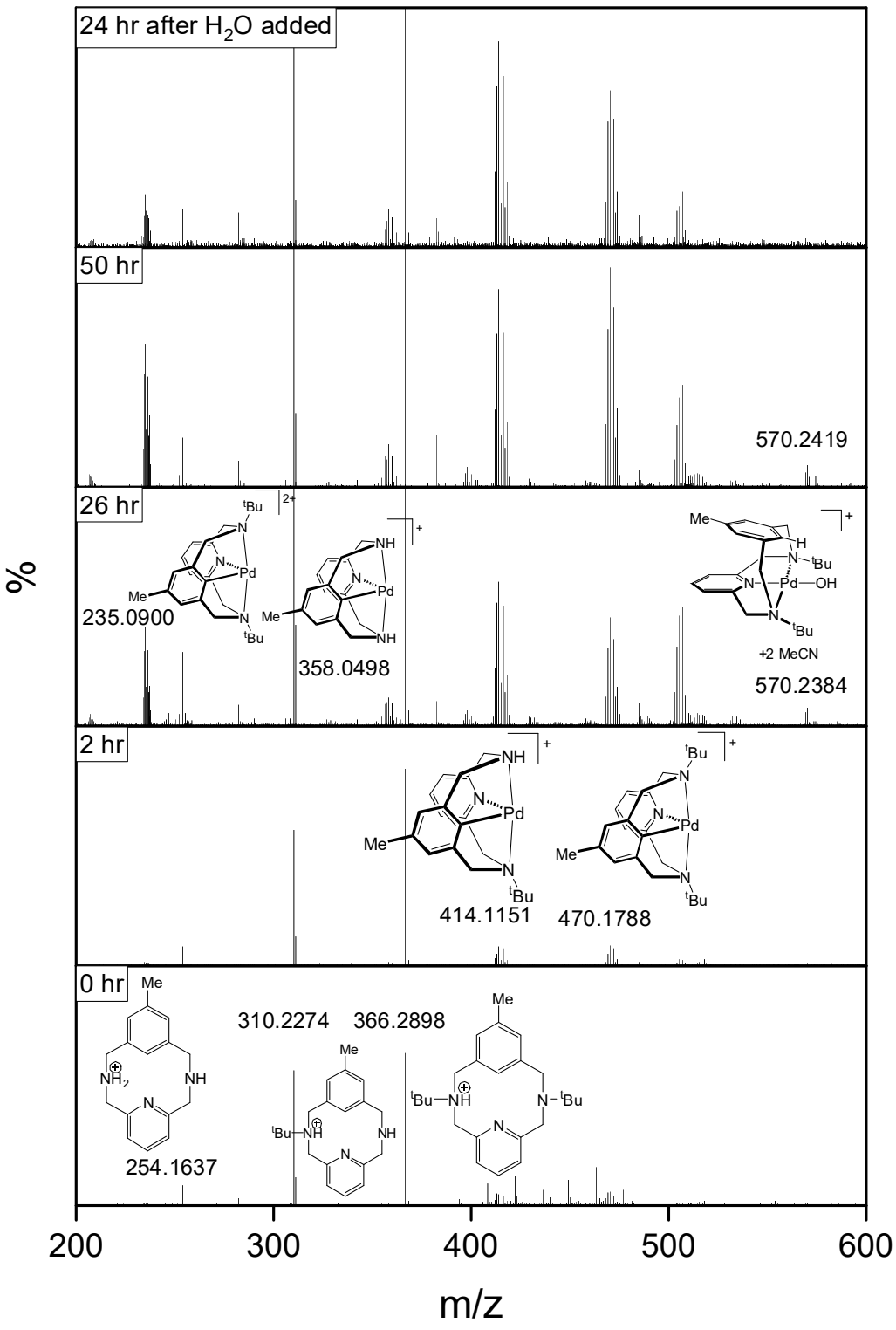


Figure S40. ESI-MS spectra for the aerobic oxidation of **1a** in MeCN according to time.

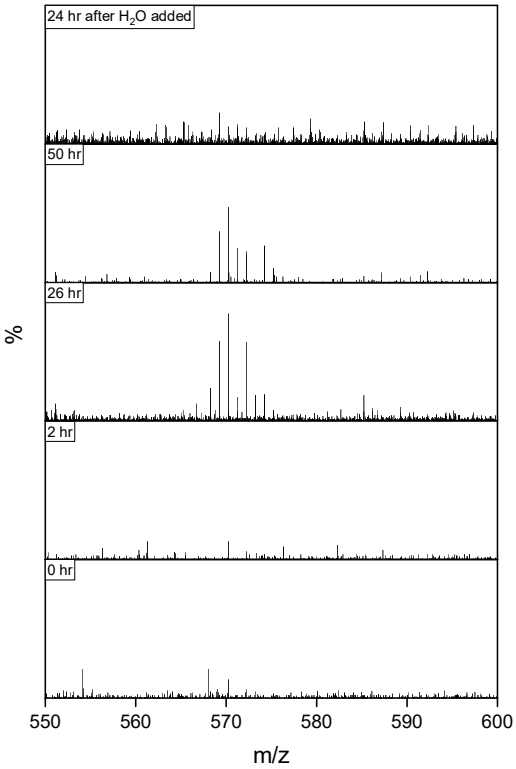


Figure S41. ESI-MS spectra for the aerobic oxidation of **1a** in MeCN in the magnified region (m/z 550~600).

b) Aerobic oxidation of **1a** in 2:8 H_2O:MeCN solvent mixture

Solution of **1a** (1.318 mM) in MeCN was prepared and 1.6 mL of solution **1a** was placed into a 4 mL quartz cuvette equipped with a septum-sealed cap and a magnetic stir bar followed by the addition of 0.4 mL of degassed DI water to make the solution 1.05 mM. Oxygen balloon was prepared and the inlet needle (22 G) connecting to the balloon and the outlet (23 G) needle were inserted orderly while the tip of inlet needle was placed in bottom of the solution and that of outlet needle was placed to the top of the headspace. Oxygen was then bubbled through the solution for 45 seconds then needles were removed in the reverse order to make the cuvette a closed system, and the reaction mixture was stirred under closed gas system. Reaction progress was monitored by UV-Vis spectroscopy, and aliquots were withdrawn periodically for ESI-MS analysis. Throughout the reaction period, no signal corresponding to a Pd–OH containing species (m/z = 570.2419) was observed by ESI-MS. Additional experiments conducted using other H_2O:MeCN ratios (1:9 and 5:5) similarly showed no detectable Pd–OH assigned signal over the course of the reaction.

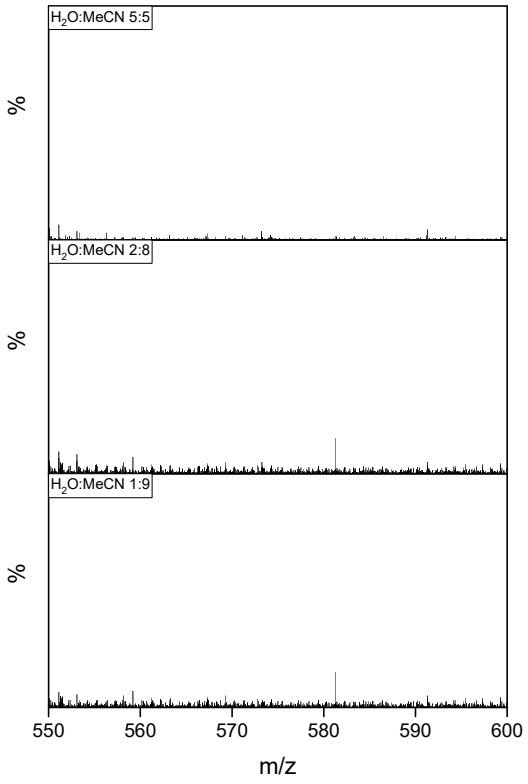


Figure S42. ESI-MS spectra for the aerobic oxidation of **1a** in H_2O:MeCN solvent mixture in the magnified region (m/z 550~600).

c) Aerobic oxidation of **1b** in MeCN

Aerobic oxidation of **1b** in MeCN was performed following the same general procedure described for **1a**. Aliquots were collected at various reaction times for ESI-MS analysis. At early reaction times (0–2h), no Pd–OH assigned signal was detected. At extended reaction times (≥26 h), a peak at m/z 556.2263 (calcd for $[(^{pH}N3CH)Pd(OH)(MeCN)_2)]^+$, 556.2268) gradually emerged and increased in intensity, becoming clearly observable after 50 h. This signal disappeared following the addition of degassed DI water (200 μL) to the reaction mixture. Additional peaks corresponding to ligand-derived fragment ions were observed at m/z 352.2749, 296.2124, and 240.1493. Signals at m/z 456.1639, 400.0995, and 344.0332 were assigned to $[(^{pH}N3C)Pd]^+$ and related fragment ions, while a peak at m/z 228.0819 was assigned to the doubly charged species $[(^{pH}N3C)Pd]^{2+}$.

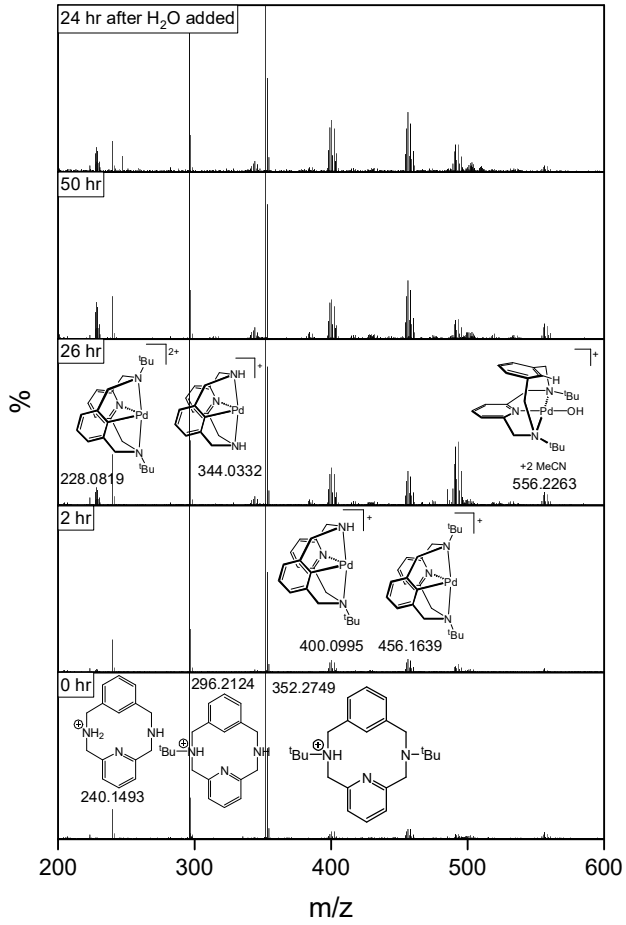


Figure S43. ESI-MS spectra for the aerobic oxidation of **1b** in MeCN according to time.

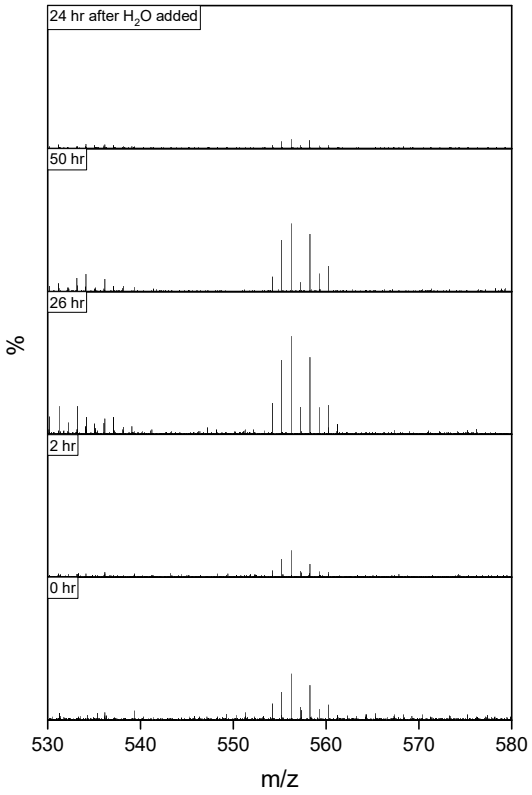


Figure S44. ESI-MS spectra for the aerobic oxidation of **1b** in MeCN in the magnified region (m/z 530~580).

d) Aerobic oxidation of **1b-D** in MeCN

Aerobic oxidation of the deuterated analogue **1b-D** in MeCN was conducted under the same conditions used for **1b**. Reaction aliquots were analyzed by ESI-MS at various time points. No Pd–OH assigned signal was observed at early reaction times. At longer reaction times (≥26 h), a peak at m/z 557.2325 (calcd for $[(^{pH}N3CD)Pd(OH)(MeCN)^2)]^+$, 557.2325) was detected and increased in intensity, becoming prominent after 50 h. As observed for **1b**, this signal disappeared upon addition of degassed water (200 μL). Fragment ions corresponding to ligand-derived species were observed at m/z 353.2809, 297.2182, and 241.1552. Peaks at m/z 456.1673, 400.1043, 344.0343 were assigned to $[(^{pMe}N3C)Pd]^+$ and related fragment ions, while a peak at m/z 228.0823 corresponded to $[(^{pMe}N3C)Pd]^{2+}$.

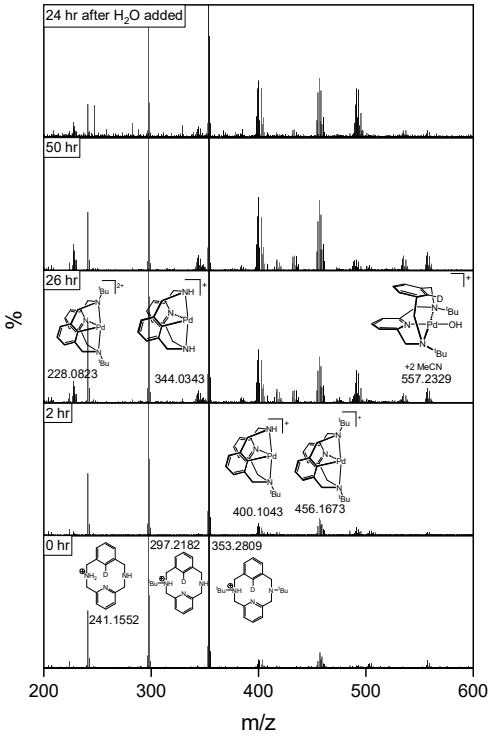


Figure S45. ESI-MS spectra for the aerobic oxidation of **1b-D** in MeCN according to time.

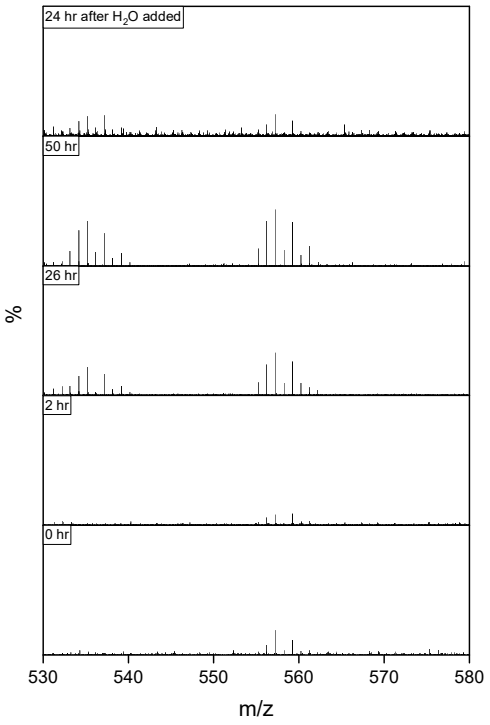


Figure S46. ESI-MS spectra for the aerobic oxidation of **1b-D** in MeCN in the magnified region (m/z 530~580).

8. X-ray Structure Characterization

General information.

Single crystals of **1a**, **1ab**, and **2a** were grown by vapor diffusion of diethyl ether into concentrated solution of acetonitrile at -35 ºC. Crystals were mounted on a Bruker D8 Venture kappa diffractometer equipped with a Photon II CPAD detector. An Iμs microfocus Mo source (λ= 0.71073 Å) coupled with a multi-layer mirror monochromator provided the incident beam. The sample was mounted on a nylon loop with the minimal amount of Paratone-N oil. Data was collected as a series of φ and/or ω scans. Data were collected at 100 K using a cold stream of N_2(g). The collection, cell refinement, and integration of intensity data was carried out with the APEXIII software.[13] A multiscan absorption correction was performed with SADABS or TWINABS-2012/1.[14] The structure was phased with intrinsic methods using SHELXT and refined with the full-matrix least-squares program SHELXL.[15] Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all non-hydrogen atoms were refined anisotropically. Software and solutions: SAINT V8.38A (2016), SHELXT (Sheldrick, 2015), XL (Sheldrick, 2008), Olex2 (Dolomanov et al., 2009).[15-17]

The deposition numbers CCDC 2331324, 2331325, and 2331326 at the Cambridge Crystallographic Data Centre CCDC contain the supplementary crystallographic data. These data are provided free of charge by the Cambridge Crystallographic Data Centre. Crystallographic details are summarized in Tables S15-23.

X-ray structure determination of 1a

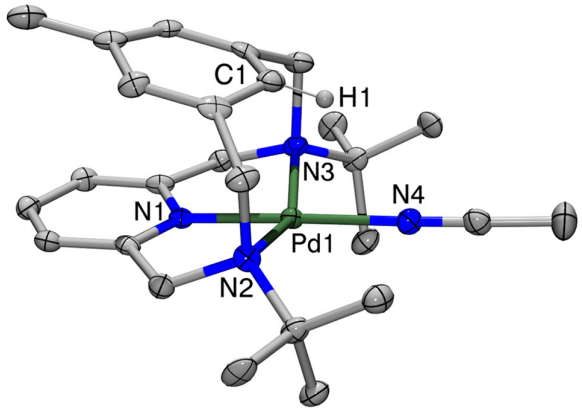


Figure S47. Solid-state structure of dication of **1a** with 50% probability ellipsoids.

Table S15. Crystal data and structure refinement for **1a.**

Empirical formula	$C_{28}H_{41}B_2F_8N_5Pd$
Formula weight	727.68
Temperature/K	100.05
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.1854(10)
b/Å	13.2252(11)
c/Å	19.5898(17)
α/°	90
β/°	105.091(5)
γ/°	90
Volume/Å^3	3048.1(4)
Z	4
ρ_{calc}g/cm^3	1.586
μ/mm^{-1}	0.686
F(000)	1488.0
Crystal size/mm^3	0.535 × 0.109 × 0.091
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.154 to 55.296

Index ranges	$-15 \leq h \leq 15, -17 \leq k \leq 15, -25 \leq l \leq 25$
Reflections collected	48647
Independent reflections	6936 [R_{int} = 0.0872, R_{sigma} = 0.0696]
Data/restraints/parameters	6936/1/411
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0768, wR_2 = 0.1967
Final R indexes [all data]	R_1 = 0.1062, wR_2 = 0.2208
Largest diff. peak/hole / e $Å^{-3}$	7.55/-1.22

Table S16. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Pd1	3143.1(4)	4199.2(3)	7233.9(2)	14.94(16)
N1	4745(4)	4569(4)	7479(3)	15.9(10)
N2	3501(4)	4038(4)	8394(3)	17.4(10)
N3	3442(4)	3952(4)	6186(3)	17.9(10)
N4	1474(4)	3871(4)	6963(3)	20.2(11)
C1	3791(5)	2350(5)	7378(3)	21.9(13)
C2	4344(5)	2426(5)	6843(3)	20.8(12)
C3	5528(5)	2365(4)	7018(3)	19.3(12)
C4	6158(5)	2311(5)	7726(3)	20.9(12)
C5	5556(5)	2420(5)	8244(3)	20.0(12)
C6	4389(6)	2477(5)	8074(3)	21.3(13)
C7	3732(6)	2905(5)	8557(3)	21.9(13)
C8	4585(5)	4610(5)	8671(3)	18.8(12)
C9	5307(5)	4661(4)	8164(3)	16.1(11)
C10	6462(5)	4861(5)	8353(3)	19.1(12)
C11	7029(5)	4945(5)	7826(3)	20.6(12)
C12	6441(5)	4811(5)	7124(3)	19.6(12)
C13	5282(5)	4611(5)	6963(3)	17.0(12)
C14	4548(5)	4507(5)	6230(3)	18.9(12)
C15	3639(6)	2799(5)	6137(3)	23.5(13)

C16	7404(6)	2262(5)	7907(4)	28.3(15)
C17	2603(5)	4442(5)	8761(3)	20.5(13)
C18	2202(5)	5467(5)	8441(3)	23.9(13)
C19	1597(5)	3729(5)	8651(3)	23.1(13)
C21	2561(5)	4328(5)	5508(3)	20.7(13)
C23	1547(5)	3599(5)	5293(3)	24.7(14)
C24	2135(5)	5357(6)	5668(3)	25.3(14)
C25	527(5)	3686(5)	6781(3)	23.5(13)
C26	-667(6)	3445(7)	6532(4)	36.6(18)
C20	3133(6)	4551(6)	9561(3)	25.0(14)
C22	3090(6)	4390(6)	4878(3)	27.8(15)
N1S	1009(8)	955(7)	5645(5)	60(2)
C1S	295(7)	1253(7)	5170(5)	48(2)
C2S	-607(7)	1639(9)	4613(5)	54(2)
B1	6287(6)	2612(7)	5248(4)	27.6(17)
F1	5610(3)	3337(3)	4814(2)	27.8(9)
F2	5574(3)	1843(3)	5379(2)	29.0(9)
F3	6867(4)	3067(4)	5873(2)	42.0(12)
F4	7039(4)	2185(4)	4905(3)	50.8(14)
B2	601(7)	3932(7)	2968(5)	33.2(18)
F5	182(5)	4148(4)	3533(3)	67.1(18)
F6	1750(4)	3714(4)	3205(3)	47.6(12)
F7	444(4)	4733(4)	2502(2)	41.7(11)
F8	35(5)	3079(5)	2639(4)	75(2)

Table S17. Bond lengths for **1a.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	N1	1.947(5)	C8	C9	1.490(8)
Pd1	N2	2.210(5)	C9	C10	1.384(8)
Pd1	N3	2.201(5)	C10	C11	1.388(8)
Pd1	N4	2.011(5)	C11	C12	1.386(8)
Pd1	C1	2.563(6)	C12	C13	1.390(8)
N1	C9	1.343(7)	C13	C14	1.488(8)
N1	C13	1.340(7)	C17	C18	1.520(9)
N2	C7	1.542(8)	C17	C19	1.517(9)
N2	C8	1.496(8)	C17	C20	1.538(8)
N2	C17	1.553(8)	C21	C23	1.538(9)
N3	C14	1.518(8)	C21	C24	1.518(9)
N3	C15	1.551(8)	C21	C22	1.535(9)
N3	C21	1.555(8)	C25	C26	1.445(9)
N4	C25	1.142(8)	N1S	C1S	1.165(12)
C1	C2	1.390(9)	C1S	C2S	1.427(12)
C1	C6	1.378(9)	B1	F1	1.400(9)
C2	C3	1.395(9)	B1	F2	1.403(9)
C2	C15	1.509(9)	B1	F3	1.382(9)
C3	C4	1.402(9)	B1	F4	1.390(9)
C4	C5	1.406(8)	B2	F5	1.364(11)
C4	C16	1.468(10)	B2	F6	1.386(10)
C5	C6	1.376(9)	B2	F7	1.380(10)
C6	C7	1.500(9)	B2	F8	1.390(10)

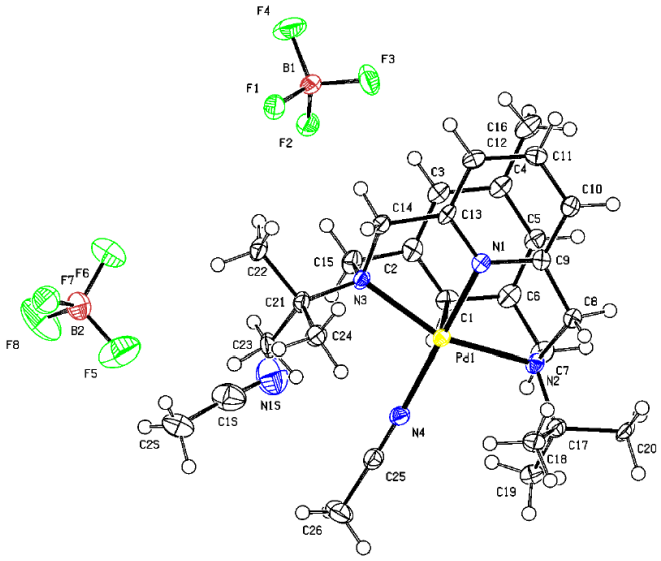


Figure S48. Projection view of **1a** with 50% probability ellipsoids.

X-ray structure determination of 1ab.

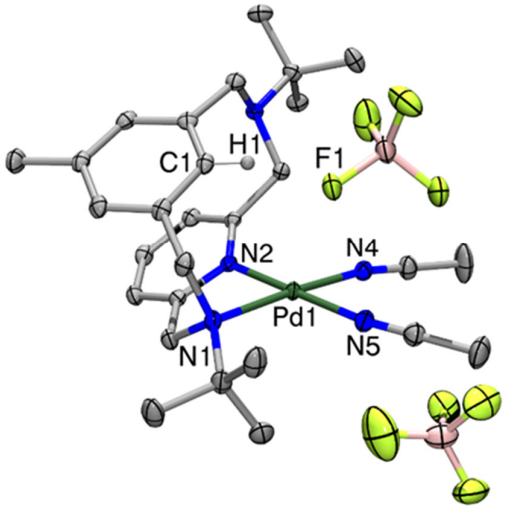


Figure S49. Solid-state structure of **1ab** with 50% probability ellipsoids. Selected distances (Å) and angles (°): H1···F1 2.473, C1–H1···F1 151.9.

Table S18. Crystal data and structure refinement for **1ab.**

Identification code	P1
Empirical formula	$C_{30}H_{44}B_2F_8N_6Pd$
Formula weight	768.73
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	7.7290(3)
b/Å	9.6870(4)
c/Å	22.8572(9)
α/°	85.0080(10)
β/°	84.3020(10)
γ/°	86.3840(10)
Volume/Å^3	1693.86(12)
Z	2
ρ_{calc}g/cm^3	1.507
μ/mm^{-1}	0.623
F(000)	788.0

Crystal size/mm^3	0.115 × 0.108 × 0.023
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.228 to 52.88
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28
Reflections collected	72887
Independent reflections	6961 [R_{int} = 0.0491, R_{sigma} = 0.0222]
Data/restraints/parameters	6961/3/464
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0273, wR_2 = 0.0623
Final R indexes [all data]	R_1 = 0.0309, wR_2 = 0.0641
Largest diff. peak/hole / e Å^{-3}	0.66/-0.55

Table S19. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1ab**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Pd1	4574.3(2)	6070.3(2)	7181.3(2)	15.67(5)
F1	7607.6(19)	8020.2(13)	7700.0(6)	31.9(3)
F4	6203(2)	9959.8(15)	7302.7(7)	44.9(4)
F3	7876(2)	10116.2(16)	8042.6(8)	48.3(4)
N2	3213(2)	4770.5(17)	7762.8(7)	15.9(3)
N1	6414(2)	4413.7(17)	7187.1(7)	19.1(4)
N3	1661(2)	6475.7(17)	9061.7(7)	16.4(3)
F2	5307(2)	9071.5(17)	8224.6(8)	56.2(5)
N4	2601(2)	7520.5(18)	7136.1(8)	21.1(4)
N5	5799(2)	7416.9(19)	6583.6(8)	22.7(4)
C2	6558(3)	4303(2)	8304.8(9)	18.3(4)
C15	1974(2)	5087(2)	8200.0(8)	15.5(4)
C14	972(3)	4045(2)	8480.5(9)	18.4(4)
C1	5697(3)	5454(2)	8546.7(9)	17.6(4)
C3	7533(3)	4461(2)	7700.3(9)	21.0(4)
C7	4584(3)	5302(2)	9060.6(9)	18.3(4)

C13	1285(3)	2687(2)	8336.3(9)	21.2(4)
C5	5372(3)	2827(2)	9141.5(9)	19.5(4)
C4	6417(3)	2999(2)	8611.3(9)	20.3(4)
C10	5290(3)	3179(2)	7274.5(9)	20.6(4)
C12	2698(3)	2359(2)	7942.9(9)	20.3(4)
C16	1779(3)	6545(2)	8410.0(8)	16.9(4)
C11	3661(3)	3431(2)	7669.6(8)	17.7(4)
C8	3423(3)	6514(2)	9265.2(9)	19.1(4)
C21	367(3)	7524(2)	9323.6(9)	19.2(4)
C25	1671(3)	8415(2)	7006.9(10)	24.8(5)
C6	4446(3)	3985(2)	9354.6(9)	19.6(4)
C27	6153(3)	8334(2)	6259.6(10)	23.9(5)
C9	5186(3)	1399(2)	9456.4(10)	26.2(5)
F5	2846(3)	6509(2)	5668.3(14)	96.4(8)
C17	7665(3)	4281(2)	6608.3(10)	25.8(5)
F6A	355(7)	7868(8)	5667(6)	49(2)
C22	-1444(3)	7214(2)	9172.3(9)	23.2(4)
C28	6628(4)	9502(3)	5843.0(12)	39.5(6)
C18	9092(3)	5314(2)	6571.1(11)	30.7(5)
C24	340(3)	7338(2)	9999.2(9)	26.5(5)
C26	487(4)	9579(3)	6846.0(14)	47.4(8)
C20	6599(3)	4516(3)	6073.9(10)	31.5(5)
C19	8540(3)	2810(2)	6607.3(11)	34.7(6)
C23	772(3)	9027(2)	9103.8(11)	27.4(5)
N6	3116(3)	11972(3)	6261.9(12)	54.9(7)
F8A	2924(5)	8908(4)	5504.4(16)	62.7(15)
C29	2974(4)	12525(3)	5811.3(13)	44.3(7)
F7A	1771(6)	7832(3)	4808.2(12)	75.2(14)
B1	6733(4)	9294(3)	7821.7(12)	30.1(6)
C30	2810(5)	13271(4)	5242.1(14)	61.8(9)
B2	2035(4)	7699(4)	5408.1(14)	42.4(7)

F8B	3364(7)	8122(8)	5095(4)	93(4)
F7B	993(7)	6880(8)	5111(3)	72(3)
F6B	900(30)	8209(18)	5812(4)	95(5)

Table S20. Bond lengths for **1ab.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	N2	2.0143(16)	C15	C16	1.525(3)
Pd1	N1	2.0759(17)	C14	C13	1.385(3)
Pd1	N4	2.0115(18)	C1	C7	1.388(3)
Pd1	N5	2.0129(18)	C7	C8	1.510(3)
F7Aa	B2	1.400(4)	C7	C6	1.394(3)
F6Aa	B2	1.378(7)	C13	C12	1.383(3)
F8Aa	B2	1.438(4)	C5	C4	1.391(3)
F1	B1	1.405(3)	C5	C6	1.391(3)
F4	B1	1.386(3)	C5	C9	1.511(3)
F3	B1	1.385(3)	C10	C11	1.495(3)
N2	C15	1.355(3)	C12	C11	1.383(3)
N2	C11	1.352(3)	C21	C22	1.528(3)
N1	C3	1.531(3)	C21	C24	1.537(3)
N1	C10	1.510(3)	C21	C23	1.539(3)
N1	C17	1.569(3)	C25	C26	1.452(3)
N3	C16	1.479(2)	C27	C28	1.455(3)
N3	C8	1.485(3)	F5	B2	1.393(4)
N3	C21	1.500(3)	C17	C18	1.527(3)
F2	B1	1.379(3)	C17	C20	1.533(3)
N4	C25	1.128(3)	C17	C19	1.538(3)
N5	C27	1.135(3)	N6	C29	1.131(4)
C2	C1	1.390(3)	C29	C30	1.446(4)
C2	C3	1.507(3)	B2	F8B	1.262(6)
C2	C4	1.395(3)	B2	F7B	1.422(6)
C15	C14	1.384(3)	B2	F6B	1.315(7)

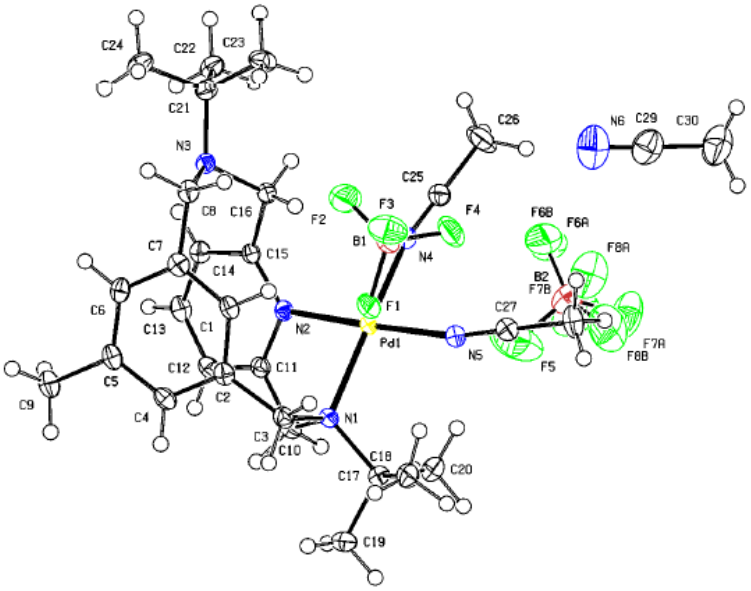


Figure S50. Projection view of **1ab** with 50% probability ellipsoids.

X-ray structure determination of 2a

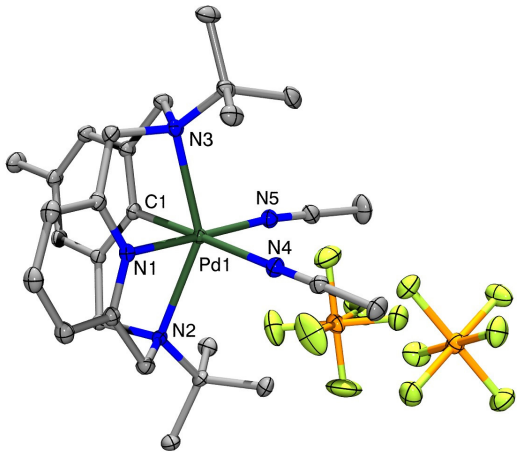


Figure S51. Solid-state structure of **2a** with 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Pd1–C1 1.959(1), Pd1–N1 2.020(1), Pd1–N2 2.396(1), Pd1–N3 2.382(1), Pd1–N4 2.163(1), Pd1–N5 2.094(1), N2–Pd1–N3 146.97(4).

Table S21. Crystal data and structure refinement for **2a**.

Identification code	P21n_a
Empirical formula	$C_{32}H_{46}F_{12}N_7P_2Pd$
Formula weight	925.10
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	18.4894(4)
b/Å	10.4350(2)
c/Å	20.2727(4)
α/°	90
β/°	96.9980(10)
γ/°	90
Volume/Å^3	3882.21(14)
Z	4
ρ_{calc}g/cm^3	1.583
μ/mm^{-1}	0.652

F(000)	1884.0
Crystal size/mm^3	0.28 × 0.151 × 0.081
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.398 to 61.132
Index ranges	-26 ≤ h ≤ 26, -14 ≤ k ≤ 14, -28 ≤ l ≤ 28
Reflections collected	153495
Independent reflections	11891 [R_{int} = 0.0442, R_{sigma} = 0.0185]
Data/restraints/parameters	11891/0/498
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0250, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0291, wR_2 = 0.0617
Largest diff. peak/hole / e Å^{-3}	0.80/-0.59

Table S22. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Pd1	7523.1(2)	2909.7(2)	5076.1(2)	11.39(3)
P2	4503.8(2)	1932.3(4)	3884.1(2)	18.91(7)
P1	6144.5(2)	3605.2(4)	1537.1(2)	23.50(8)
F7	5295.5(5)	1482.0(10)	4213.4(5)	26.42(19)
F9	4440.6(6)	686.7(9)	3419.8(5)	30.5(2)
F12	4561.5(5)	3187.1(10)	4348.0(5)	29.1(2)
F11	4144.1(5)	1160.6(10)	4444.3(5)	30.7(2)
F8	4862.4(6)	2699.8(10)	3324.2(5)	31.1(2)
F10	3707.6(5)	2386.3(11)	3558.0(5)	32.3(2)
F4	5491.3(6)	2646.6(11)	1619.6(6)	36.5(2)
F3	6093.4(8)	3244.1(11)	762.4(5)	43.9(3)
F2	6704.4(6)	2427.9(12)	1688.7(6)	42.9(3)
N1	7916.8(6)	3792.2(10)	5932.0(5)	13.19(19)
F1	6809.2(8)	4548.3(13)	1440.5(7)	53.6(3)
N5	7133.3(6)	1986.9(11)	4186.3(6)	16.6(2)
N4	6507.9(6)	2446.3(12)	5449.7(6)	17.2(2)
F5	5596.1(8)	4754.2(12)	1355.1(8)	60.4(4)

F6	6221.1(10)	3933.3(15)	2298.8(6)	64.7(4)
N2	7301.8(6)	5138.4(11)	4851.0(5)	13.23(19)
N3	8350.7(6)	1326.1(11)	5561.4(6)	14.4(2)
C1	8440.2(7)	3373.2(12)	4745.1(6)	13.2(2)
C5	9681.6(7)	3945.9(13)	4184.5(7)	16.8(2)
C2	8551.5(7)	4636.8(12)	4571.1(6)	13.5(2)
C11	8600.4(8)	3701.0(14)	6995.0(7)	18.8(3)
C3	8040.8(7)	5662.7(12)	4755.8(6)	14.0(2)
C10	8407.1(7)	3185.6(12)	6366.7(6)	14.6(2)
C7	8947.6(7)	2410.5(13)	4708.0(7)	15.0(2)
C4	9179.3(7)	4909.7(13)	4277.6(7)	16.1(2)
C15	7109.8(7)	5526.9(13)	5515.2(6)	15.8(2)
C8	8805.5(7)	1125.0(13)	5004.7(7)	16.6(2)
C23	6602.2(8)	6980.7(13)	4270.2(7)	19.2(3)
C14	7626.8(7)	4933.2(12)	6065.4(6)	14.5(2)
C6	9573.2(7)	2708.9(13)	4418.0(7)	17.1(2)
C25	5956.0(7)	2184.4(13)	5607.3(6)	15.6(2)
N7	3288.7(10)	7179.9(15)	2762.3(8)	36.5(3)
C13	7816.0(7)	5501.4(13)	6681.5(7)	17.8(2)
C19	7475.8(8)	-447.8(14)	5253.8(7)	20.9(3)
C16	8786.7(7)	2039.6(13)	6112.2(7)	16.1(2)
C17	8037.8(7)	83.1(12)	5800.1(7)	16.7(2)
C12	8298.8(8)	4864.1(14)	7150.0(7)	19.3(3)
C21	6731.0(7)	5522.7(13)	4280.8(7)	15.6(2)
C22	6015.3(7)	4827.7(14)	4347.0(7)	20.7(3)
C27	6829.8(8)	1492.8(13)	3735.0(7)	18.7(3)
C18	7654.8(8)	363.2(14)	6413.8(7)	19.7(3)
C9	10339.4(8)	4264.7(15)	3845.5(8)	22.9(3)
C20	8641.7(8)	-920.7(14)	5967.0(8)	22.7(3)
C26	5247.7(8)	1881.1(15)	5806.5(7)	21.7(3)
N6	5476.2(10)	7708(2)	2667.8(9)	48.2(5)
C24	6999.7(8)	5115.6(14)	3626.8(7)	19.9(3)
C29	5993.9(10)	7633.0(18)	2417.6(8)	31.7(4)

C30	6662.8(10)	7542.6(19)	2109.2(9)	32.5(4)
C31	3702.2(10)	6371.9(16)	2836.9(9)	31.6(4)
C28	6437.9(10)	876.9(18)	3152.6(8)	31.1(4)
C32	4223.3(13)	5325(2)	2944.9(12)	50.0(6)

Table S23. Bond lengths for **2a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	N1	2.0201(11)	C1	C2	1.3867(18)
Pd1	N5	2.0937(11)	C1	C7	1.3828(18)
Pd1	N4	2.1626(12)	C5	C4	1.3973(19)
Pd1	N2	2.3955(11)	C5	C6	1.3977(19)
Pd1	N3	2.3819(11)	C5	C9	1.5052(19)
Pd1	C1	1.9588(12)	C2	C3	1.5047(18)
P2	F7	1.6034(10)	C2	C4	1.3966(18)
P2	F9	1.6008(10)	C11	C10	1.3887(18)
P2	F12	1.6081(10)	C11	C12	1.388(2)
P2	F11	1.6016(10)	C10	C16	1.5090(19)
P2	F8	1.5977(10)	C7	C8	1.5062(18)
P2	F10	1.6099(10)	C7	C6	1.3951(18)
P1	F4	1.5927(11)	C15	C14	1.5105(18)
P1	F3	1.6066(11)	C23	C21	1.5397(19)
P1	F2	1.6118(12)	C14	C13	1.3883(18)
P1	F1	1.6050(12)	C25	C26	1.4516(19)
P1	F5	1.5845(13)	N7	C31	1.136(2)
P1	F6	1.5711(12)	C13	C12	1.391(2)
N1	C10	1.3433(16)	C19	C17	1.527(2)
N1	C14	1.3467(17)	C17	C18	1.5327(19)
N5	C27	1.1370(18)	C17	C20	1.5384(19)
N4	C25	1.1392(18)	C21	C22	1.5292(19)
N2	C3	1.5060(16)	C21	C24	1.5315(19)
N2	C15	1.4900(16)	C27	C28	1.457(2)
N2	C21	1.5209(16)	N6	C29	1.139(3)
N3	C8	1.5020(17)	C29	C30	1.455(3)

N3	C16	1.4938(17)	C31	C32	1.456(3)
N3	C17	1.5231(17)			

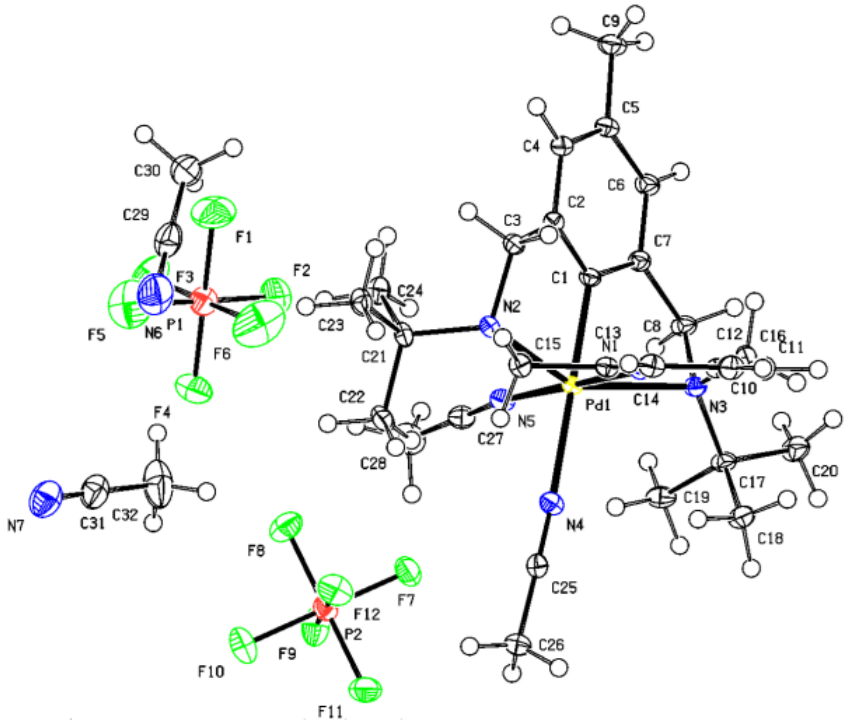


Figure S52. Projection view of **2a** with 50% probability ellipsoids.

9. Computational Details

Geometry optimizations of all compounds were carried out using the atomic coordinates derived from energy minimized or crystal structures. No constraints were forced on the geometry optimization. Geometry optimizations and frequency calculations were performed at the B3LYP level of theory utilizing the Stuttgart/Dresden ECP (SDD) basis set using the Gaussian 16 package.[18, 19] Water or acetonitrile were used as the solvent, and solvation was modeled utilizing the SMD variant of the IEFPCM SCRF model.[20]

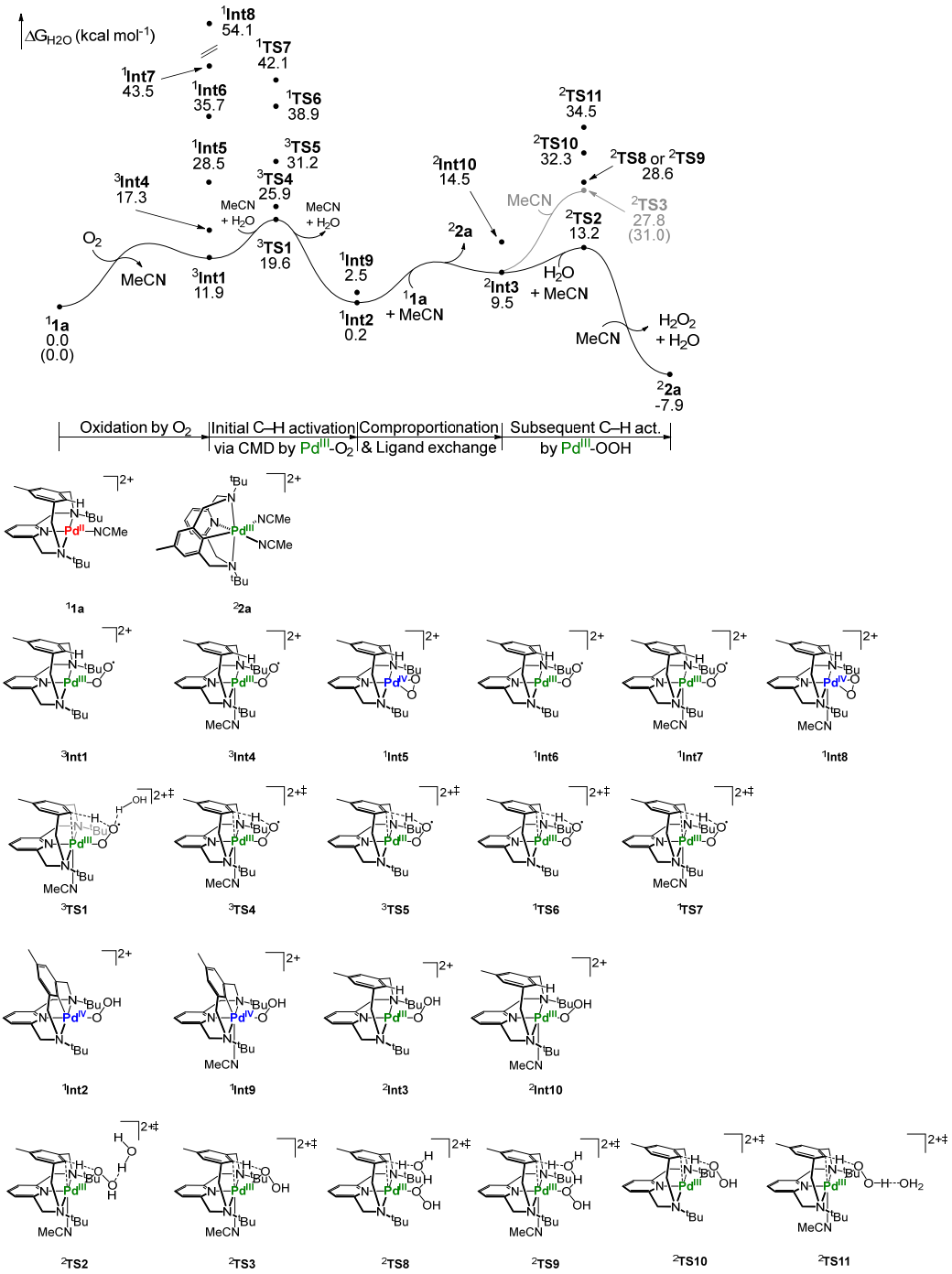


Figure S53. The overall energy profile for the proposed mechanism of the aerobic C–H activation of **1a** by molecular oxygen to afford complex **2a** with possible optimized structures in the reaction pathway. The solvation calculations were utilized using H_2O as solvent. Gibbs energies in the parenthesis on ^{1}**1a** and ^{2}**TS3** stand for Gibbs energies in acetonitrile using solvent model density (SMD) method. Several binuclear Pd-O_2 species were also examined. In these calculations, we did not identify a binuclear structure competitive in energy with the mononuclear Pd^{III}-superoxo intermediate ^{3}**Int1**. However, because the absence of a low-energy optimized structure does not exclude all possible binuclear pathways, the present calculations

should be viewed as supporting a mononuclear pathway rather than definitively ruling out binuclear species.

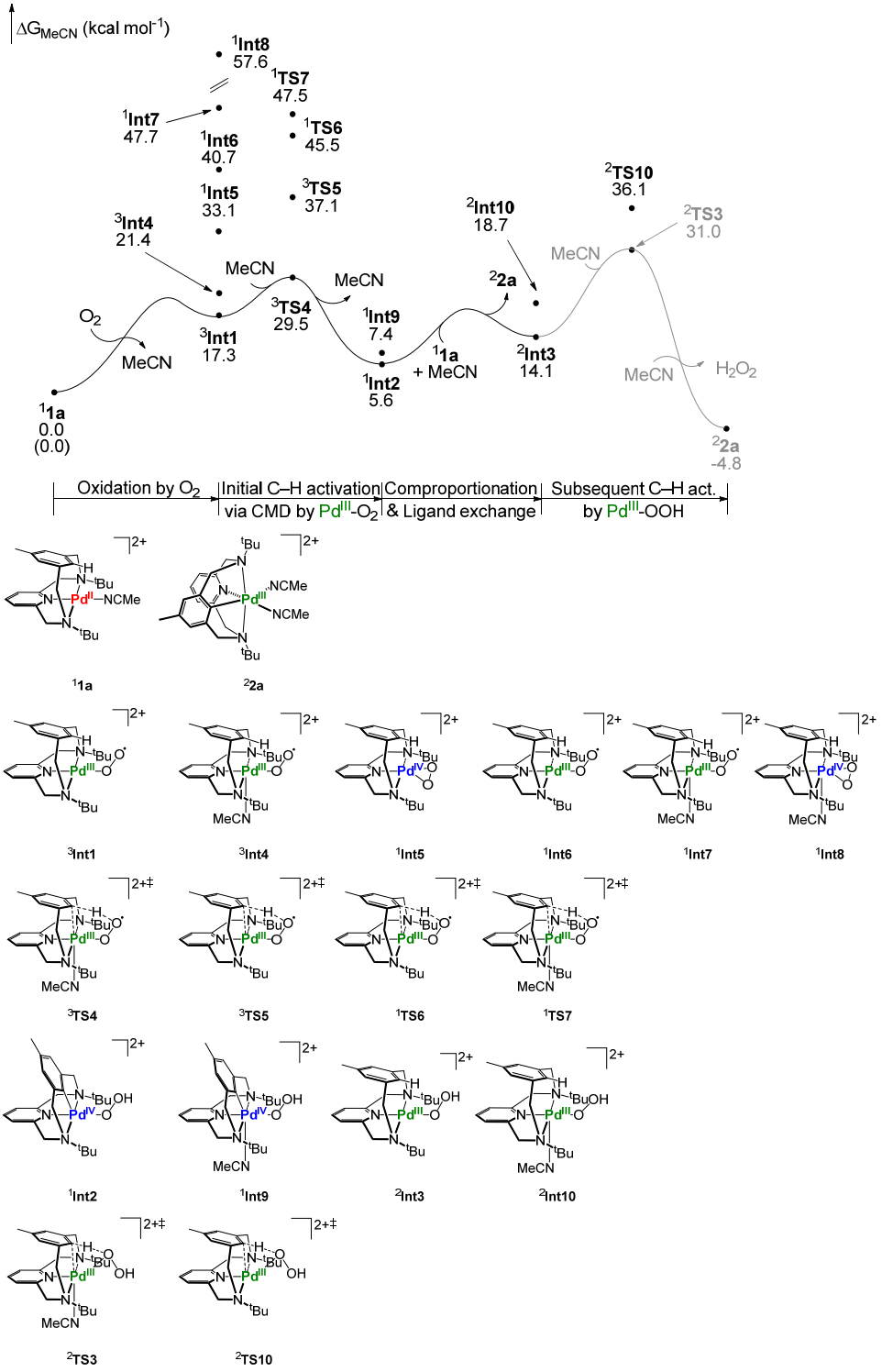


Figure S54. The overall energy profile for the proposed mechanism of the aerobic C–H activation of **1a** by molecular oxygen to afford complex **2a** with possible optimized structures in the reaction pathway. The solvation calculations were utilized using MeCN as solvent.

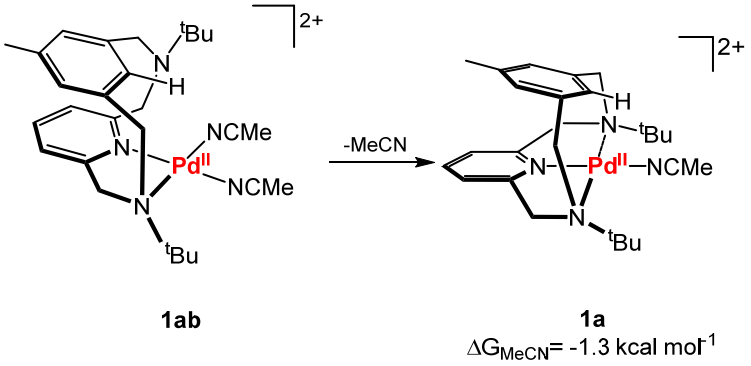
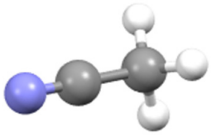


Figure S55. DFT calculation of a reaction from **1ab** to **1a**.

Table 24. Computed energy components for DFT-optimized structures (unit: Hartree)

	E°	G°	E^{o}_{H2O}	G^{o}_{H2O}	E^{o}_{MeCN}	G^{o}_{MeCN}
MeCN	-132.728543	-132.707055	-132.734784	-132.713296	-132.738698	-132.71721
O_2	-150.315314	-150.332079	-150.316673	-150.333439	-150.319219	-150.335984
H_2O	-76.4143925	-76.411943	-76.4327383	-76.4302888	-76.42478	-76.4223305
H_2O_2	-151.540687	-151.53823	-151.558742	-151.556285	-151.552451	-151.549994
1a	-1359.9134	-1359.36852	-1360.1349	-1359.59002	-1360.15503	-1359.61015
1ab	-1492.67044	-1492.08813	-1492.88364	-1492.30134	-1492.90758	-1492.32527
2a	-1492.06552	-1491.49579	-1492.26789	-1491.69816	-1492.29394	-1491.7242
Int1	-1377.44668	-1376.94425	-1377.69369	-1377.19126	-1377.70378	-1377.20135
Int2	-1377.46628	-1376.96181	-1377.71435	-1377.20987	-1377.72455	-1377.22007
Int3	-1378.07377	-1377.55877	-1378.31526	-1377.80025	-1378.32469	-1377.80969
Int4	-1510.21068	-1509.66882	-1510.43776	-1509.8959	-1510.45385	-1509.91199
Int5	-1377.42313	-1376.91907	-1377.66886	-1377.1648	-1377.68016	-1377.1761
Int6	-1377.41281	-1376.90806	-1377.65803	-1377.15328	-1377.66877	-1377.16402
Int7	-1377.42313	-1509.62685	-1510.39793	-1509.85422	-1510.41386	-1509.87015
Int8	-1510.15625	-1509.61071	-1510.3828	-1509.83726	-1510.39983	-1509.85429
Int9	-1510.24043	-1509.69356	-1510.46639	-1509.91953	-1510.4812	-1509.93433
Int10	-1510.83679	-1510.28253	-1511.05978	-1510.50552	-1511.07376	-1510.5195
TS1	-1586.632563	-1586.074244	-1586.853091	-1586.294772	-	-
TS2	-1587.24941	-1586.67897	-1587.46706	-1586.93781	-	-
TS3	-1510.81633	-1510.26759	-1511.03314	-1510.4844	-1511.04867	-1510.49993
TS4	-1510.19689	-1509.65859	-1510.42035	-1509.88204	-1510.43739	-1509.89909
TS5	-1377.41082	-1376.91309	-1377.65819	-1377.16046	-1377.66755	-1377.16982
TS6	-1377.39361	-1376.89218	-1377.64954	-1377.14811	-1377.65787	-1377.15644
TS7	-1510.16773	-1509.62316	-1510.40092	-1509.85634	-1510.41505	-1509.87047
TS8	-1454.49272	-1453.96194	-1454.73079	-1454.20002	-	-
TS9	-1587.26927	-1586.69582	-1587.48674	-1586.91329	-	-
TS10	-1378.03125	-1377.52364	-1378.27146	-1377.76385	-1378.28221	-1377.7746
TS11	-1454.48266	-1453.95506	-1454.71818	-1454.19057	-	-

MeCN

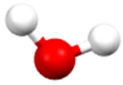


N 5.5680598759 12.6864924038 14.2665710494
C 5.3935282127 13.1806832524 13.2085792272
C 5.1743228127 13.7969884929 11.8931842919
H 6.0134260403 13.5740617146 11.2247877947
H 5.0855111869 14.8844943827 11.9931044537
H 4.2541518715 13.4106797536 11.4407731832

O_2

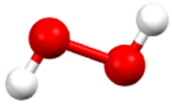
O -0.6598290403 -0.0576369197 -0.0623905243
O 0.6076110403 -0.0348210803 -0.1007734757

H_2O



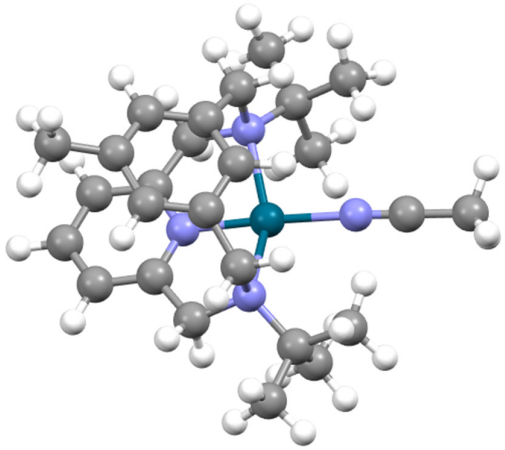
O -9.5416291519 0.0944263867 0.0
H -10.2857367331 0.7271266467 0.0
H -9.880727115 -0.8215530334 0.0

H_2O_2



O -9.4992630197 0.1086547399 -0.0143002461
O -10.1382655698 -1.2672286801 0.0140817919
H -10.318326844 0.6587166432 0.006965041
H -9.3191855664 -1.817286703 -0.0066455868

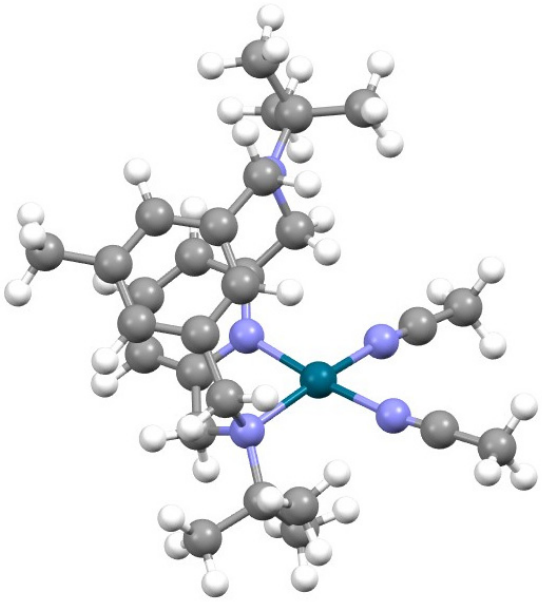
1a



Pd 0.1165277466 5.5756699565 13.641224224
N 1.9547648935 6.1347477913 14.1136777455
N -0.0254717688 5.3396366456 15.9118419426
N 1.1192067191 5.2040601095 11.6193379645
N -1.8311540455 5.2075898463 13.1332660649
C 0.972246353 3.1391318777 13.9462230291
C 1.9574084853 3.1917280694 12.9435854214
C 3.3039818521 3.0134576139 13.3109078962
C 3.6712970626 2.8636056627 14.6728168257
C 2.6789669234 3.088712866 15.6611230305
C 1.330629139 3.2671974761 15.3003542888
C 0.2624544499 3.8260102139 16.2170051334
C 1.1443468576 6.1858018908 16.4147525938
C 2.269354129 6.331609212 15.4249665968
C 3.5625412468 6.7345962975 15.7833853933
C 4.5287627852 6.9103024943 14.776134128
C 4.1900141231 6.65859784 13.434208779
C 2.8837660042 6.2573353566 13.1242661568
C 2.3991505148 6.0346047043 11.716394335
C 1.4940697919 3.6791087267 11.5866761962
C 5.0967520492 2.5374919698 15.0623042212
C -1.348947431 5.8231904504 16.6427661312
C -1.7573936127 7.1909055329 16.0468998949
C -2.4919287276 4.7991865813 16.4326926042
C 0.3430045641 5.6253824959 10.3005124245
C -0.7704478419 4.5996676118 9.9731373155
C -0.2840858477 7.0197795961 10.5345071067
C -2.9545824409 5.0887862889 12.8374077756
C -4.358944221 4.9430600796 12.4672615716
C -1.1167230929 5.9626446572 18.1748380345
C 1.3083023906 5.6775416265 9.0814532469
H -0.0788265588 3.093780742 13.6680691702
H 4.0807963946 2.9959341858 12.548486811
H 2.9745946686 3.1290475235 16.7080256234
H 0.5363363856 3.7478865706 17.2753328428
H -0.6773849961 3.298653974 16.0609464684
H 0.7669579094 7.188092747 16.6335835321
H 1.5220739597 5.7763522095 17.3582185954
H 3.8081994453 6.9076480785 16.825859099
H 5.5337604678 7.2294145375 15.0342553507
H 4.9250610657 6.7724397013 12.6444022332
H 3.1892185981 5.5734714819 11.1133745337
H 2.1994515845 7.016051613 11.2784793071
H 0.5914157984 3.1489452584 11.2868644095
H 2.255133494 3.5418334214 10.8100664932
H 5.2326197966 1.4492037448 15.1320864238
H 5.3617502497 2.9557672058 16.039831411
H 5.8186380461 2.9027054426 14.3232078381
H -0.9913882915 7.9651016643 16.1680102454
H -2.6506529791 7.5532257496 16.5678053208
H -1.9977480609 7.1126426772 14.9820241652
H -2.5478801564 4.4323522406 15.4056641064
H -3.4425041454 5.2911277304 16.6665840295

H -2.4108603368 3.9395523672 17.1055572187
H -0.3802922199 3.7032477703 9.4806725771
H -1.4703146467 5.0637846592 9.2695019676
H -1.3357667342 4.2929010031 10.8556109544
H -1.0250634641 6.9997860004 11.3397436732
H -0.7917605781 7.340006364 9.6178498826
H 0.4536554771 7.7954953169 10.768701636
H -4.8202985744 5.9281880677 12.3293513271
H -4.9081843276 4.4069695625 13.2503174414
H -4.4521174972 4.3799989245 11.5310331748
H -0.7360601911 5.0392143502 18.6260482741
H -2.0823544088 6.172302184 18.6483440112
H -0.4505671762 6.7885710013 18.4423536347
H 2.0334817546 6.4954410867 9.1326576771
H 0.7093632346 5.8453436108 8.1793900028
H 1.8468479616 4.7344766904 8.9337614647

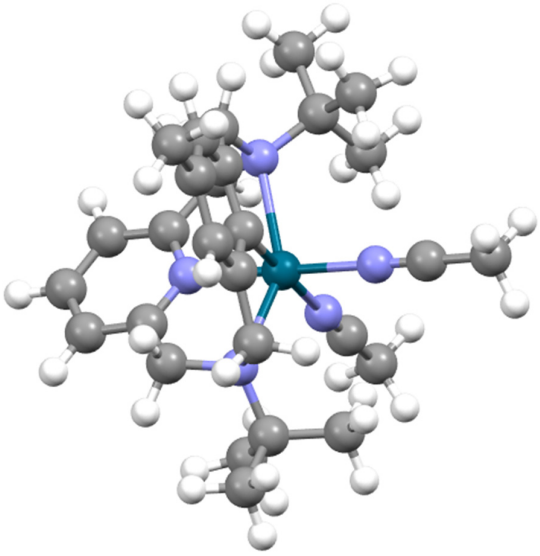
1ab



Pd 5.5148487055 7.2373891226 16.2231650767
N 4.4327491415 6.0797983776 17.495611394
N 6.7996208985 5.5339062042 16.2065596898
N 3.7624085216 8.0414482632 20.4572285399
N 4.0016227893 8.611399803 15.9883005551
N 6.6349901436 8.5465017196 15.0982644453
C 7.2391578749 5.656145892 18.7728411316
C 3.5973518146 6.5073841872 18.4952888813
C 2.7815549303 5.5654433105 19.1477520783
C 6.6995409005 6.8618520429 19.2634216318
C 7.8279229372 5.6033240849 17.3819812118
C 5.9868996416 6.8928318399 20.4734149055
C 2.8631038266 4.2049540707 18.8202213978
C 6.5922660676 4.5363190696 20.863437494
C 7.2010766718 4.5074333456 19.5865963802
C 5.8002656006 4.3831310536 16.389854049
C 3.8526628304 3.7801412848 17.9142714613
C 3.6070822799 7.9632142232 18.9901472059
C 4.6458027277 4.7423379188 17.2868747729
C 5.1996018426 8.134335353 20.870463248
C 2.7922810731 8.97705858 21.1777041141
C 3.1301192742 9.3372757647 15.7111117334
C 5.9527286812 5.7280257454 21.2682953587
C 7.1777769671 9.4130749003 14.5341193831
C 6.6288600008 3.3238249328 21.7714940074
C 7.5924043071 5.269253331 14.8342564045
C 1.3411312367 8.4864550364 20.9414916082
C 7.8764983668 10.4844332329 13.8295658436

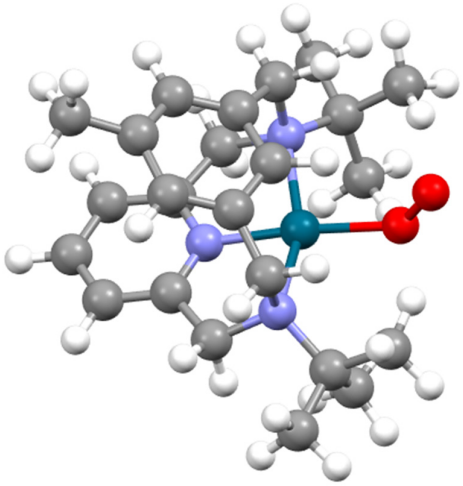
C 8.8581880554 6.1571286438 14.7553156888
C 3.0467676097 8.9189522607 22.7053830675
C 2.0330833415 10.2365611248 15.3617863903
C 6.6607782178 5.5599641497 13.63257274
C 8.0548555066 3.7837516284 14.7609522091
C 2.9511246939 10.4447524224 20.6866904325
H 2.1330173856 5.9176034218 19.9397088882
H 6.7948796159 7.7753899869 18.6762467564
H 8.4747222305 4.7257153055 17.2814430108
H 8.4246510424 6.4951953287 17.187326341
H 2.214990106 3.4811695838 19.3045640326
H 7.6624337393 3.5823227671 19.2428654997
H 5.4261301211 4.1063692053 15.4020460683
H 6.3225177942 3.5119445245 16.7977784814
H 4.0204450564 2.7256010821 17.7217046851
H 4.4048613831 8.5153828492 18.4731925476
H 2.6605794602 8.4289837472 18.7008381806
H 5.2323247598 8.2487649112 21.9533012676
H 5.6806387961 9.0274754142 20.4269058582
H 5.4234856884 5.7500423855 22.2187036649
H 5.7279382597 3.2534349747 22.3913582341
H 7.486437454 3.3797928564 22.4561102997
H 6.7284542159 2.3907099276 21.2055200104
H 1.0575212794 8.4446452997 19.8818481544
H 0.6392369685 9.172685362 21.428441644
H 1.1944863139 7.4925713274 21.3812401441
H 7.4338742606 10.6429524728 12.8391889712
H 8.9350578861 10.2289651352 13.7010100488
H 7.8118551615 11.419962828 14.3973483594
H 8.6679249652 7.1990519818 15.0177615268
H 9.2257677731 6.1337016554 13.7232443132
H 9.6680294379 5.7837950441 15.3889067341
H 3.1182728466 7.8811386438 23.0525761274
H 2.2058642409 9.3885893275 23.22736433
H 3.9484602516 9.4608350856 23.010956165
H 2.0372920066 10.4400380107 14.2845718152
H 2.1302617985 11.1876500976 15.8980688007
H 1.0703302721 9.7821326685 15.6232878631
H 5.7166490588 5.0048732684 13.6686073988
H 7.1727864722 5.2429330972 12.7169189519
H 6.4311662246 6.622554237 13.5284098959
H 8.6259486989 3.4666254382 15.6401353231
H 8.7244211235 3.6872654166 13.8991218137
H 7.2330661741 3.0800119802 14.6002639945
H 3.977652453 10.8042647068 20.8314898482
H 2.2872474046 11.1097647275 21.2514745786
H 2.6927923408 10.5536909959 19.6236148395

2a



Pd 12.5959137116 3.0509836767 10.208581889
N 13.1827487604 3.9766995141 11.9418717653
N 12.1322284337 2.0909959022 8.3895267877
N 12.2742370442 5.4519215369 9.7272697125
N 14.0292636383 1.3076724222 11.220202727
C 14.3947866806 3.5052778403 9.5118251501
C 16.8999959932 4.0621620603 8.4005088761
C 14.6664568724 4.8198254691 9.1172636987
C 14.2502635478 3.8842671002 14.0767834594
C 13.6897489469 5.9380903117 9.4342562151
C 13.989304486 3.3192199546 12.8168821546
C 15.3486588747 2.4782590746 9.4643805238
C 15.9280241876 5.07926746 8.5384031985
C 11.8497513642 5.8777256551 11.1093958841
C 14.9973788089 1.1284865108 10.0612062232
C 10.9954562854 7.4057589396 8.6846926188
C 12.6805777058 5.2170486086 12.1991260753
C 16.6059896802 2.7703746059 8.8994602215
C 12.935553646 5.82912562 13.4345059319
C 12.4758937804 -0.5886208829 10.579690182
C 14.7034298101 2.0635601385 12.3411056121
C 13.3825204358 -0.021070981 11.6973579431
C 13.7085496464 5.1431849639 14.3915250579
C 11.2576642088 5.8748230634 8.6282603225
C 9.9218956235 5.1204656009 8.8249107674
C 11.9147220663 1.5596218207 7.3739141123
C 12.5087603038 0.257283154 12.9454105839
C 18.2363135026 4.3522515599 7.7461548723
C 14.4752113895 -1.0683091234 12.0507257386
C 11.8298198546 5.4971788465 7.2391889732
C 11.6470114533 0.9010598367 6.0976533041
H 14.8820432717 3.3596572262 14.786421706
H 13.672677526 6.6776554514 8.6302709462
H 14.0572169769 6.4713980476 10.321783324
H 16.1683570107 6.0882395323 8.2072259257
H 10.7985768829 5.6076955203 11.246329105
H 11.9234155214 6.9669678269 11.2280062153
H 14.5092221127 0.4931289552 9.3176829369
H 15.9052356956 0.6069914419 10.3934773267
H 10.439447047 7.7011823862 9.5818460961
H 10.3888256338 7.697647484 7.8200546462
H 11.920965643 7.9921750966 8.641043042
H 17.3685217412 1.9952578298 8.8513235741
H 12.5440899411 6.8195831976 13.6426213547
H 11.9989420033 -1.5057864209 10.9430091572
H 13.0339651003 -0.8600121601 9.6770079368
H 11.6881500697 0.1200310852 10.3091761354
H 15.6907665464 2.3901345097 11.9897255244
H 14.8875843694 1.4083128966 13.1960961419
H 13.9050261099 5.5950152861 15.3589934275
H 9.4377526842 5.3442678577 9.7823815457
H 10.0615208755 4.039070143 8.7434086372
H 9.2241147169 5.4334627257 8.0402816249
H 11.8129832235 1.0836071367 12.7717119863
H 13.0992167931 0.4797204827 13.840617337
H 11.9215380233 -0.6388692059 13.1738316955
H 18.19049285 4.1653415565 6.6642958793
H 19.0314234837 3.7170727021 8.1513787925
H 18.5358165488 5.396889801 7.8827240406
H 13.9966189556 -1.9538806898 12.4839488884
H 15.1935791787 -0.696402543 12.7914767306
H 15.0316832472 -1.4007402248 11.1679034854
H 11.0350198832 5.5960520888 6.4916119122
H 12.1918218672 4.4657166748 7.2229748988
H 12.6459634854 6.1522555136 6.9191489076
H 10.8450515714 1.4204244044 5.5604514327
H 11.3410124301 -0.1389958769 6.2587675351
H 12.5464712703 0.9079836639 5.4711138353
N 10.5777668516 2.5840404592 11.0011374874
C 9.5066814833 2.3234787167 11.3900301216
C 8.1677864038 1.9929696415 11.8747254606
H 7.9992389723 0.9111806229 11.8224337968
H 7.4055584559 2.4926358054 11.265879409
H 8.0468577988 2.3129510908 12.9160204557

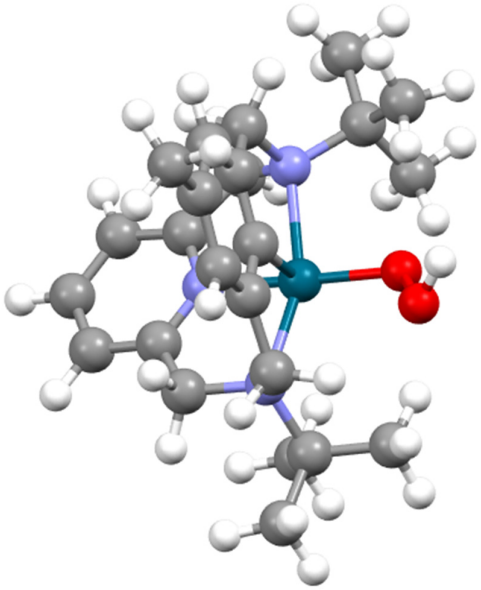
Int1



Pd -0.7020643376 0.268605263 -0.1849183855
N 1.0895990721 1.074653818 0.262275379
N -0.8796939829 0.1769577299 2.0448516667
N 0.2334981859 0.0641061403 -2.209005351
O -2.6232161663 -0.2448233256 -0.6738240056
C 0.1301128041 -1.8970614118 0.0899847476
C 1.1364285875 -1.899181616 -0.9266965754
C 2.4573878099 -2.1608550198 -0.5637532189
C 2.8120734987 -2.3651294249 0.8055886194
C 1.834150145 -2.0984659208 1.813108747
C 0.5084966645 -1.8361333855 1.4681947423
C -0.5525135032 -1.2997293386 2.4081780649
C 0.2461183428 1.0994426651 2.5434385868
C 1.3851214702 1.2951519123 1.5693018302
C 2.6614558252 1.7579038758 1.9196035503
C 3.6103914055 1.9661231388 0.8980050093
C 3.2800136502 1.6954200321 -0.4455260728
C 1.9896049852 1.2342342002 -0.7420919419
C 1.4698960813 0.9769134688 -2.137872763
C 0.6799109288 -1.4238845251 -2.2915157063
C 4.2056271945 -2.7904718151 1.1821929429
C -2.2637195695 0.6549818899 2.6968707875
C -2.7038275996 1.9405686648 1.9597394252
C -3.3570299675 -0.4290023571 2.5459679145
C -0.6483230537 0.4895308741 -3.4779203758
C -1.6889074252 -0.600732341 -3.8268115335
C -1.3772796876 1.8040362978 -3.1165160885
O -3.0775485623 -1.482359759 -0.7598718523
C -2.0692752567 0.9235157743 4.215615711
C 0.267629737 0.6849857075 -4.7185901139
H -0.9003609608 -2.1328542879 -0.1738428522
H 3.2365384592 -2.2107629316 -1.3208500684
H 2.1410853363 -2.1011588104 2.8564374279
H -0.2488076895 -1.3472996984 3.4593605422
H -1.4763581973 -1.8664908345 2.2906454284
H -0.1941013286 2.0821304386 2.7306518968
H 0.6205877017 0.7327853018 3.5049784932
H 2.9106062064 1.9563497584 2.9568986312
H 4.6021212824 2.330994045 1.1477428339
H 4.0073295216 1.8455829639 -1.2366609931
H 2.2621533447 0.5699875745 -2.7749977262
H 1.1885678546 1.9436200479 -2.5632242932
H -0.1887573272 -1.9975332247 -2.6154188733
H 1.4603066463 -1.5179526773 -3.0541786303
H 4.2577412796 -3.8900942743 1.2240100853
H 4.4995225014 -2.4244778923 2.1715772739
H 4.9518587811 -2.468646138 0.4481565941
H -1.9401328017 2.7278897881 1.9547490187
H -3.5779963528 2.3585370892 2.4710977399
H -3.0051743619 1.7295648835 0.928418504
H -3.4405158139 -0.8310606471 1.5361066955

H -4.3208080379 0.036341537 2.7798306577
H -3.2333932061 -1.2545453023 3.2550631053
H -1.2443456976 -1.4589035323 -4.3420845774
H -2.4091216943 -0.1610891446 -4.5254578127
H -2.2608168959 -0.9528346635 -2.9680879494
H -2.1472964318 1.6407877131 -2.355362845
H -1.8842838229 2.1832299566 -4.0106735078
H -0.7043053348 2.6015377653 -2.778555025
H -1.6437388498 0.0604582326 4.7418043863
H -3.0575383209 1.1026016046 4.6530576148
H -1.4653793846 1.8089465454 4.4362139258
H 0.9123283932 1.5671373448 -4.6596439298
H -0.3779724224 0.8277229158 -5.5920308039
H 0.8862903476 -0.1967096596 -4.9250617076

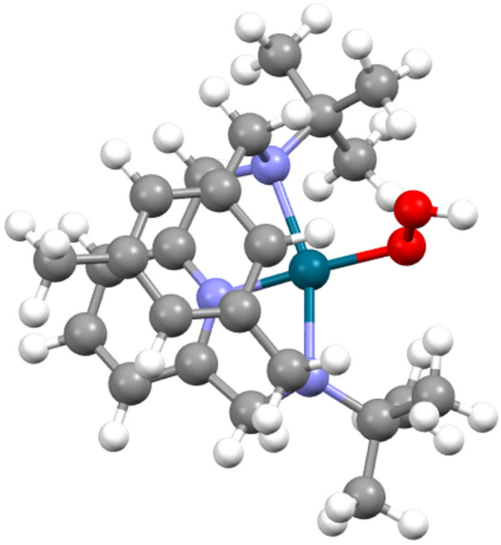
Int2



Pd -0.7019493781 -0.0358585133 0.0329667247
N 0.0498230037 1.8308441422 -0.006932919
N -0.2165109575 0.1129811982 2.1551643469
N -0.4387977897 0.2062761802 -2.146908178
O -1.662508112 -1.7629752612 -0.0693178389
C 1.0885859517 -0.8467579672 -0.0229250915
C 1.7047758834 -0.8846164501 -1.2617534642
C 2.9607874316 -1.5348938583 -1.2777915359
C 3.5199083885 -2.0742803653 -0.0912633706
C 2.8227753626 -1.9473446136 1.141562852
C 1.5617229415 -1.3203360944 1.1983507303
C 0.6709342102 -1.1246556592 2.4113220387
C 0.682673431 1.366917276 2.2861945174
C 0.5766361433 2.3382993591 1.1339327291
C 1.0704617139 3.6514790787 1.1336423422
C 1.0366188629 4.3856874828 -0.0694207879
C 0.5300006926 3.8024728574 -1.2520038594
C 0.0300608127 2.4962749484 -1.1928860836
C -0.590641554 1.7243502616 -2.3373591585
C 1.0426328148 -0.1886653087 -2.4348635528
C 4.8537238609 -2.79284103 -0.1352102324
C -1.4743775639 0.2220223183 3.1260908522
C -2.2411898963 1.5120095061 2.7525482702
C -2.4166931066 -0.9872042757 2.9464434533
C -1.4610470845 -0.5600508164 -3.1076773836
C -1.1132410652 -2.0672487142 -3.1442698545
C -2.8940619222 -0.36489399 -2.5583439316
O -1.2682016863 -2.8222308789 0.8786648066
C -0.9937219925 0.2611598278 4.6013365979
C -1.3529721038 0.0208807087 -4.5431268737
H -1.0733384854 -3.5843164585 0.2776652827

H 3.510978295 -1.621897296 -2.2123375717
H 3.2702196565 -2.3446823139 2.0501068486
H 1.2411427305 -0.9829741377 3.335733374
H 0.0094694497 -1.9837275421 2.5271479509
H 0.47326438 1.8637235198 3.2339289434
H 1.722564916 1.0238726492 2.3317972244
H 1.483932428 4.0873558336 2.0372634418
H 1.4178809919 5.4020949777 -0.0911066654
H 0.5253776972 4.3556435817 -2.1853764185
H -0.1461410239 2.0246628279 -3.2908410261
H -1.6585996377 1.9546029878 -2.3904112803
H 1.0705280789 -0.8089613268 -3.3312446252
H 1.5925991564 0.7313842246 -2.6663470798
H 4.7073826112 -3.8782248521 -0.2217099775
H 5.4374959191 -2.6170555524 0.7747330896
H 5.4583200079 -2.4759999515 -0.9907558266
H -1.6655738317 2.4307755989 2.9081361916
H -3.1305787782 1.5844892545 3.386909939
H -2.5965012215 1.4875463806 1.7129435193
H -2.7959714684 -1.0797383031 1.9268855202
H -3.2761855156 -0.8372883207 3.6091786706
H -1.9583691348 -1.9385761789 3.225849551
H -0.2512502267 -2.2911854422 -3.781503651
H -1.9664823816 -2.6012577158 -3.5761737318
H -0.9465253254 -2.4698039321 -2.1449103314
H -3.0430645706 -0.8869621448 -1.6094940139
H -3.5986093359 -0.7989524952 -3.2765698328
H -3.1832299967 0.6875874728 -2.44853906
H -0.4731917715 -0.6581125767 4.8895137361
H -1.879930441 0.336296405 5.2409533752
H -0.3577325892 1.1184482194 4.8475099169
H -1.7782258329 1.0254931997 -4.6361472481
H -1.9281161767 -0.6288241695 -5.2120103147
H -0.3236178052 0.0332823079 -4.922441166

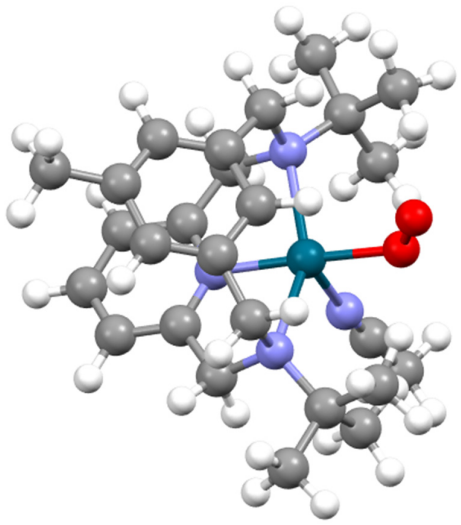
Int3



Pd -0.6889705292 0.239226381 -0.1182993559
N 1.1017868579 1.0335857775 0.3162539979
N -0.844278052 0.146424072 2.1128192016
N 0.2167951597 0.0642750937 -2.1542385418
O -2.5558987112 -0.3055171975 -0.5600021752
C 0.1510429791 -1.8646065329 0.1386458977
C 1.1310295603 -1.905905686 -0.9125080794
C 2.4429563462 -2.2398849877 -0.5917830139
C 2.8256500656 -2.4682220019 0.7700558716
C 1.8908017638 -2.169368914 1.8140308295
C 0.5739884983 -1.8380881825 1.5112948963
C -0.461471534 -1.3112424975 2.483828544
C 0.2560617238 1.100975805 2.5968062831

C 1.3961433591 1.2836773729 1.620316013
C 2.6668156313 1.7657932933 1.961440822
C 3.61272689 1.969157908 0.9354998072
C 3.2804175764 1.684738833 -0.404254222
C 1.9948763307 1.2046604665 -0.6930481835
C 1.4704738553 0.9494987256 -2.0876594719
C 0.633669051 -1.4259927435 -2.2609813724
C 4.2085464726 -2.9559667808 1.1018187138
C -2.240448946 0.5815911983 2.7552584137
C -2.7088657882 1.858223725 2.0196554166
C -3.2965493514 -0.5311681739 2.563518996
C -2.0684205364 0.8413243238 4.2762094043
C -0.6829286984 0.528867439 -3.3952273758
C -1.7483981572 -0.5377316969 -3.7311030986
C -1.381931575 1.8439275701 -2.9820851467
C 0.2101254632 0.735615741 -4.6499098536
H -0.8827837647 -2.1397285367 -0.0961678655
H 3.1972220924 -2.3298276046 -1.3698814959
H 2.2295977199 -2.2053116379 2.8466856329
H -0.1152365789 -1.3390943086 3.5225602995
H -1.3712126526 -1.9070613252 2.406946376
H -0.201521026 2.0815402807 2.7528097986
H 0.6319036449 0.7693446459 3.5705776652
H 2.9139312729 1.9844170599 2.9951355774
H 4.6012720248 2.3468298466 1.1788477998
H 4.0014107009 1.8411686951 -1.1999618372
H 2.2546809202 0.5252862158 -2.7238790044
H 1.2106886707 1.920823537 -2.5160548667
H -0.2608468159 -1.9825865193 -2.5429415723
H 1.382470632 -1.5351953923 -3.0528692723
H 4.2112889488 -4.057664444 1.1366315464
H 4.5482082441 -2.6109317829 2.0839836745
H 4.9459565334 -2.6649635818 0.3464813657
H -1.9750213951 2.6733800644 2.0384695912
H -3.6085740178 2.2409432237 2.5141514378
H -2.9792027506 1.6373840759 0.9815391826
H -3.3158792971 -0.8992817108 1.5370750678
H -4.2809303036 -0.0991071562 2.774418473
H -3.1685026312 -1.3645522197 3.2630976542
H -1.6374717324 -0.0202048048 4.8008811671
H -3.0631409231 1.0056705066 4.7049190546
H -1.4762968792 1.7322670563 4.5084082638
H -1.3300526288 -1.390216834 -4.2784444724
H -2.4844487071 -0.073502713 -4.3970050094
H -2.2810472511 -0.8939159513 -2.8498011467
H -2.1340782208 1.6590145738 -2.2081557321
H -1.904174125 2.2559556232 -3.8527001575
H -0.6889420916 2.6223614439 -2.6380134297
H 0.8700072679 1.6069127214 -4.5902200566
H -0.452392631 0.9034032359 -5.5060276917
H 0.8105165302 -0.1514832204 -4.8862780152
O -2.6631956174 -1.7889466528 -0.8317891679
H -3.6356108672 -1.9390707412 -0.7433300522

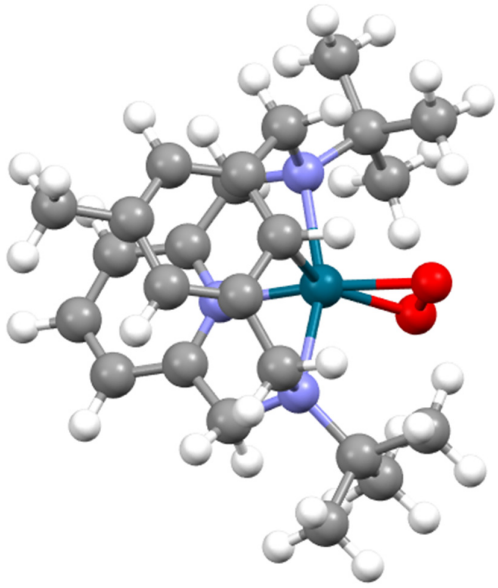
Int4



Pd -0.8260515681 0.4265588898 -0.1656835611
N 1.0315272765 1.0816497322 0.2920289747
N -0.9084653054 0.1722060345 2.2310984756
N 0.2292461725 0.1094046917 -2.3084976311
O -2.7178901472 -0.1038521538 -0.6334762418
C 0.0956527601 -1.6995239545 0.0965002837
C 1.0964943033 -1.7840026328 -0.9237288416
C 2.4022381759 -2.1366107534 -0.5851994078
C 2.7664184173 -2.3799958479 0.7709181074
C 1.8111111625 -2.1015170814 1.7910706749
C 0.5014487772 -1.7484842027 1.4685313858
C -0.5202013641 -1.2943262646 2.478538821
C 0.2322668222 1.0995340037 2.6303086799
C 1.3378040368 1.2830944244 1.6009377221
C 2.6247255638 1.7272927156 1.9419310977
C 3.567470859 1.9388727532 0.9171566861
C 3.2204830065 1.6910028307 -0.4250794879
C 1.922133199 1.2475216612 -0.7211300885
C 1.4344839689 1.0269561615 -2.1456089565
C 0.6706391074 -1.3629187934 -2.3063450125
C 4.142488391 -2.8816225928 1.1206998577
O -3.0089749962 -1.4108475123 -0.6900965269
N -1.519200302 2.5337701893 -0.3664036881
C -1.9887096282 3.5957584343 -0.4977510824
C -2.5980956869 4.9130596975 -0.6674926627
H -0.9392989493 -1.941352278 -0.156983731
H 3.1588683956 -2.2367543048 -1.3598575966
H 2.1159198336 -2.1749507063 2.8323725364
H -0.1551554963 -1.4082841302 3.5062514953
H -1.4277530592 -1.8884078371 2.3709643666
H -0.1993431263 2.0864199959 2.8212498555
H 0.6763355966 0.7629686131 3.5753949192
H 2.8856209637 1.9042481053 2.9803586157
H 4.566431608 2.2860748097 1.1632577714
H 3.9429948783 1.8399146696 -1.2210213069
H 2.2693465627 0.6615356157 -2.7564697399
H 1.1577161004 2.0058415837 -2.5478639331
H -0.189121319 -1.955486244 -2.6192098475
H 1.4722391644 -1.506110942 -3.0407771336
H 4.1419436996 -3.9826375583 1.1385406595
H 4.4648379763 -2.549959574 2.1133166006
H 4.8941098368 -2.5781120305 0.3844228393
H -2.9926444173 5.0203127336 -1.6846753049
H -1.8622134431 5.7059821742 -0.4922612418
H -3.4263317247 5.0417529473 0.039100457
C -2.227090266 0.5303442166 3.0378445243
C -2.7880696886 1.8799418589 2.5399040608
C -3.31299486 -0.5495446099 2.804453886
C -1.9135782549 0.6124240713 4.5584642707
H -2.0584588467 2.6974068062 2.563468486
H -3.6130460449 2.1730415068 3.1984578163

H -3.187253841 1.7840315782 1.5273752284
H -3.4336354973 -0.8033912723 1.7482244046
H -4.2714920067 -0.1457575162 3.1483251051
H -3.1419355658 -1.4645675184 3.3810039385
H -1.4568479262 -0.3056121152 4.9455804938
H -2.8587325491 0.7456010923 5.0963325084
H -1.2761031642 1.4634704193 4.8215473651
C -0.5478507943 0.4435816205 -3.651382479
C -1.626915001 -0.6314844842 -3.9332140859
C -1.2626528605 1.8048715535 -3.5102492988
C 0.4478966309 0.4854729604 -4.8447406038
H -1.2134905077 -1.5625900714 -4.334498464
H -2.3019664988 -0.239817512 -4.7019454128
H -2.2379295271 -0.854615446 -3.0549272495
H -2.0953455297 1.7340509602 -2.8064324135
H -1.673233089 2.0804311094 -4.4878362438
H -0.6003098351 2.6222397446 -3.2031033374
H 1.1443031594 1.3295562573 -4.7957431555
H -0.1294221237 0.6036148218 -5.7683690381
H 1.0221514058 -0.4422831045 -4.9481741646

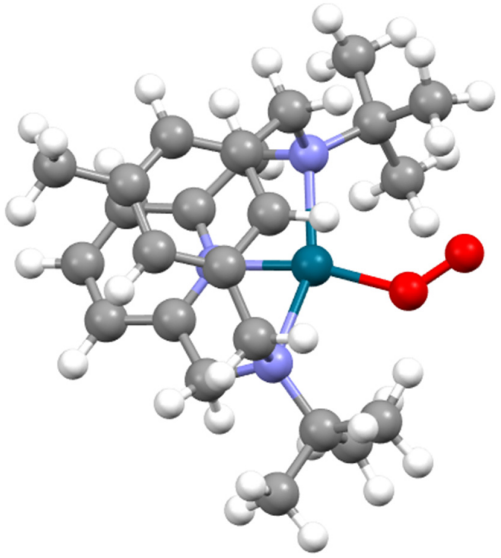
Int5



Pd -0.7009769285 0.2014903861 -0.1922575334
N 1.0563757831 1.0916631278 0.2465682567
N -0.8900934466 0.1500051265 2.0539950683
N 0.2404957728 0.0350536548 -2.2348017199
O -2.4443549422 1.2319951648 -0.6816703486
C 0.1642055929 -1.8579397466 0.0904825783
C 1.1757342622 -1.8790577397 -0.9185384319
C 2.4967957608 -2.1329807431 -0.5525825877
C 2.8465797044 -2.3301627936 0.8175043766
C 1.8639640698 -2.0736334811 1.8210768239
C 0.539427012 -1.8188248142 1.4687626671
C -0.5289044049 -1.3152600511 2.4123752318
C 0.222855227 1.0989600043 2.5392628096
C 1.3343461097 1.3576204585 1.5485915982
C 2.574502869 1.9183215918 1.8875806793
C 3.504897673 2.1774494831 0.8612758226
C 3.1939110225 1.8598073933 -0.4761847232
C 1.9401317013 1.3006131158 -0.7628497062
C 1.4518680549 0.9841576696 -2.1574537209
C 0.7249669714 -1.4374157753 -2.2922752931
C 4.241547182 -2.7430455734 1.1999363358
O -2.6359173077 -0.1812599094 -0.6891416396
H -0.8589850281 -2.145976979 -0.1748924129
H 3.2771938407 -2.1851319847 -1.3078405219

H 2.1643613008 -2.0807870328 2.8660113529
H -0.2135884228 -1.3530919535 3.4588094671
H -1.4409987823 -1.9039175996 2.3046016663
H -0.2482239553 2.057708942 2.7654417614
H 0.6341659208 0.714788921 3.4787701733
H 2.808400695 2.1543930999 2.9205929325
H 4.4668375012 2.6194854208 1.1024372502
H 3.9069313853 2.0506158906 -1.271623644
H 2.2675461381 0.5713045922 -2.7604098384
H 1.1528768842 1.9247394651 -2.6246758837
H -0.1213304289 -2.0388542802 -2.6270960861
H 1.5214145985 -1.5154729797 -3.0375866033
H 4.2983734097 -3.842257741 1.2476862749
H 4.5301296379 -2.3706174122 2.1882618069
H 4.9875004826 -2.421446804 0.4659293483
C -2.2827515579 0.5624921294 2.7738388184
C -2.6779452569 1.9990524561 2.3615591253
C -3.39934869 -0.4283944108 2.3717376954
C -2.0755211628 0.4984365571 4.3144955605
H -2.0043593365 2.7726143892 2.7484307036
H -3.6587889284 2.2113090588 2.8008150572
H -2.7744210108 2.1031806021 1.2805665967
H -3.4751006341 -0.5553885878 1.2908988121
H -4.3527211151 -0.0152886062 2.7181061668
H -3.3003481013 -1.4061358051 2.8562929585
H -1.831233153 -0.5059203327 4.6757112758
H -3.0290597685 0.774909795 4.7784919969
H -1.3292449228 1.2081110536 4.6861411002
C -0.6144948959 0.3820252128 -3.5674479661
C -1.7974446286 -0.6034227351 -3.7084375822
C -1.1423215026 1.8330694848 -3.4859801818
C 0.3212103242 0.2349949056 -4.8016605148
H -1.4857668677 -1.6085919086 -4.0135257387
H -2.4458348454 -0.2332898621 -4.5097579469
H -2.4022654799 -0.6617766985 -2.8025219333
H -1.7362068991 2.0040947701 -2.5876725947
H -1.7985921233 1.9956338959 -4.3478494628
H -0.3570818638 2.5942284668 -3.5617715376
H 1.1667835311 0.9305358687 -4.7951313425
H -0.2760492999 0.4763789224 -5.6882299603
H 0.6927792725 -0.7852687354 -4.942563693

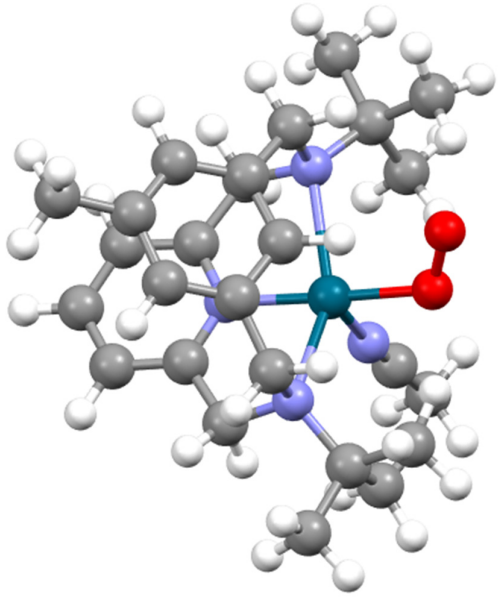
Int6



Pd -0.7519568579 0.268638403 -0.1976911667
N 1.0643262261 1.0161079801 0.2429186047
N -0.903099373 0.1591950925 2.0742940071
N 0.2205813705 0.0423960653 -2.2466596289
O -2.6939505685 0.0830514826 -0.3910499137
C 0.1354206914 -1.9017110025 0.0846022621

C 1.1504045256 -1.8864207757 -0.9157516116
C 2.4719783432 -2.1264701835 -0.5348726569
C 2.8118212884 -2.3261760403 0.8370535885
C 1.8145396751 -2.0860453984 1.8293314644
C 0.48869566 -1.8433066355 1.4644898654
C -0.5894638436 -1.3285201764 2.3945715343
C 0.2523514559 1.0461602796 2.5506166684
C 1.3648524415 1.2505813217 1.5479511164
C 2.6302992994 1.753037692 1.8858614655
C 3.5650379396 1.9930698633 0.8601854239
C 3.2274936214 1.7210379249 -0.4806060992
C 1.9502189046 1.2206946084 -0.7670273815
C 1.4263944429 0.9852442682 -2.1628456053
C 0.7103176279 -1.4325178239 -2.2915279661
C 4.2098863851 -2.7197647026 1.2323648005
C -2.2527536893 0.630495854 2.7985192579
C -2.688670477 1.9812772154 2.1849569896
C -3.3762749637 -0.4193671923 2.6089158575
C -0.6226529075 0.4067132904 -3.5602899752
C -1.6007344232 -0.7387846 -3.9151775774
C -1.3974397561 1.7135148595 -3.2771453606
O -3.4145608965 -0.2858391356 -1.4240881485
C -1.9991554559 0.7904614191 4.3248287231
C 0.3362418376 0.6019450858 -4.7695876672
H -0.8965065409 -2.1252948751 -0.1960252592
H 3.2609154448 -2.1618114788 -1.2825972752
H 2.103397333 -2.090825637 2.877796175
H -0.3050913941 -1.4095583331 3.4490450372
H -1.5145486205 -1.8856758246 2.24274606
H -0.1604097131 2.0318950154 2.7796708574
H 0.6558257156 0.6494068476 3.4888888091
H 2.8782474409 1.9599861754 2.9218851667
H 4.546545209 2.3887907296 1.1028350878
H 3.9377189647 1.9035573252 -1.2803986252
H 2.2254511179 0.6170046057 -2.814955917
H 1.1141535793 1.9545474508 -2.5607266142
H -0.13092431 -2.0357025742 -2.632228295
H 1.5125528961 -1.5120289061 -3.0331160925
H 4.2882938339 -3.8179034528 1.26982135
H 4.4802078928 -2.3515259538 2.2276183049
H 4.9587638491 -2.3759272255 0.511093987
H -1.9123845622 2.7547931836 2.226676255
H -3.5384751684 2.3644430531 2.7605043805
H -3.0217120808 1.8708819943 1.150208436
H -3.4949785444 -0.744126459 1.5742405906
H -4.3219017043 0.0478942815 2.9046614782
H -3.2488279582 -1.2942181754 3.2557698103
H -1.1039366722 -1.5603916999 -4.442231266
H -2.3561443674 -0.3391190392 -4.6005306666
H -2.1449712404 -1.1288723514 -3.053443452
H -2.1759943137 1.574682442 -2.5225745913
H -1.8976667978 2.0302497332 -4.1988886529
H -0.7517821625 2.5455160103 -2.9715373363
H -1.5955346104 -0.1196922533 4.783802293
H -2.9655002774 0.9820847323 4.8041793696
H -1.3516941619 1.6356379166 4.5784011227
H 0.9445207875 1.5096369103 -4.7099709508
H -0.2813947531 0.697209944 -5.6694165881
H 0.9935873654 -0.261150151 -4.929670859

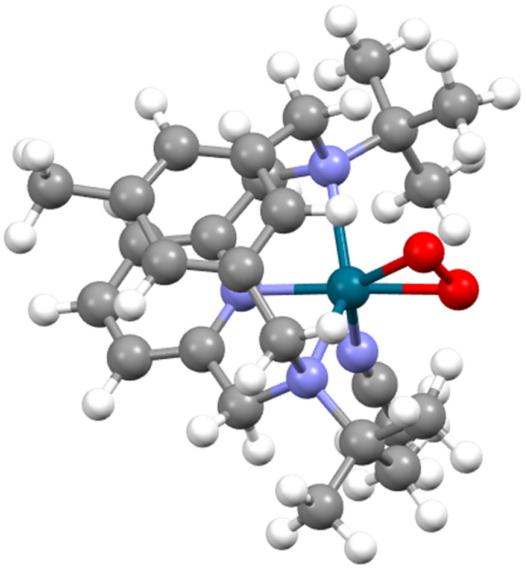
Int7



Pd -0.8641514911 0.4787612794 -0.1293434296
N 1.0045515336 1.1308977222 0.2667803662
N -0.9044614837 0.2587602913 2.2041195038
N 0.2267417013 0.0749559124 -2.3756056164
O -2.6843704158 -0.2004572811 -0.5625451149
C 0.0727430162 -1.6532963094 0.1065787642
C 1.0716959111 -1.7680234246 -0.9134576806
C 2.3698162962 -2.1496403008 -0.5660833329
C 2.7319056383 -2.3812069062 0.7898096118
C 1.7817171393 -2.0730545507 1.8073314774
C 0.4813693371 -1.6957336859 1.4795244905
C -0.5328942631 -1.2122168685 2.4794311259
C 0.240301584 1.1836659614 2.6070640682
C 1.3380408195 1.3451000847 1.5684853604
C 2.6371041151 1.7622481123 1.8898993741
C 3.5734887 1.9289901513 0.8507436338
C 3.2047099343 1.6576401357 -0.4800105127
C 1.8915416562 1.2427817792 -0.7580965362
C 1.4096583687 1.0079171423 -2.1835843017
C 0.6639841261 -1.3898591606 -2.3135050464
C 4.0983792256 -2.9040578078 1.1465903489
O -2.6831345103 -1.3871538621 -1.1962004316
N -1.5764411275 2.5184535947 -0.4644303754
C -2.0479052667 3.5661047309 -0.6758586331
C -2.6559050084 4.866491509 -0.9479933254
H -0.9625071296 -1.9158574536 -0.1540432522
H 3.1206259689 -2.2833793912 -1.341347659
H 2.0845359176 -2.1425064637 2.8495852939
H -0.1722506949 -1.3048127589 3.510116309
H -1.4497207154 -1.7945170658 2.3837132293
H -0.1862722198 2.1722011046 2.7978804027
H 0.6806113281 0.8409691409 3.5509925072
H 2.9140716515 1.9492353476 2.9223241301
H 4.5840750236 2.2545058406 1.0781757421
H 3.923545519 1.7644899857 -1.2859361384
H 2.2630091331 0.6634236876 -2.7826175389
H 1.1213495947 1.9836917873 -2.5864633451
H -0.1932968083 -1.9905365284 -2.6162030845
H 1.4774702333 -1.5671080761 -3.0296054865
H 4.0710290103 -4.003080582 1.2100754429
H 4.439186359 -2.540913735 2.1222201095
H 4.8497364596 -2.6492253683 0.3920222426
H -2.9877771296 4.918629096 -1.991560752
H -1.9380756076 5.6747611577 -0.7678486512
H -3.5269619958 5.021248634 -0.3005613253
C -2.2400442081 0.6354783304 2.9797538194
C -2.7606268866 2.0078531239 2.5000202497

C -3.3402378005 -0.4135381829 2.6906188798
C -1.9554012122 0.6800214854 4.5089076378
H -2.0133750341 2.8083244807 2.5364899303
H -3.5800717206 2.3112686726 3.1606067145
H -3.1614217586 1.9371559719 1.4864163226
H -3.4263197253 -0.6334455339 1.6212640871
H -4.3017339168 0.0049199357 3.0077493418
H -3.2121919026 -1.3449897217 3.2509998716
H -1.5462000775 -0.2615144931 4.8910380439
H -2.9064451914 0.844454184 5.0271569888
H -1.289289401 1.5005555007 4.7966782812
C -0.4978824207 0.3798698033 -3.7452755712
C -1.5211042322 -0.7294951425 -4.0851457984
C -1.2603931283 1.7187073291 -3.6331149313
C 0.5451274461 0.4575768555 -4.9010676432
H -1.052548487 -1.6350919542 -4.4847068474
H -2.1891637154 -0.353676056 -4.8678974905
H -2.1492047928 -0.9977043972 -3.2264741717
H -2.109355418 1.6239485555 -2.9511476651
H -1.6511675333 1.9799314066 -4.6226459783
H -0.631291749 2.5557818298 -3.3083908996
H 1.2015446693 1.3315395715 -4.8284150651
H 0.0029800809 0.5433999655 -5.848911682
H 1.1628326824 -0.4455261293 -4.9690843895

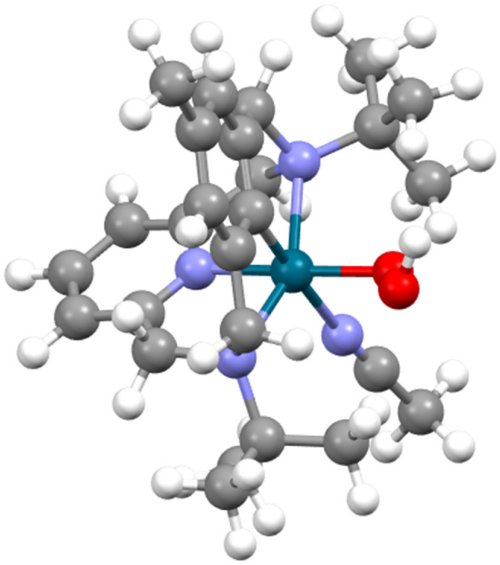
Int8



Pd -0.9561938955 0.5395863461 -0.2900424179
N 0.9516791103 0.9484152252 0.2034922327
N -0.9948399414 0.1207963354 2.0530532175
N 0.1647458275 -0.0229810026 -2.3131358429
O -2.913109752 0.2619150142 -0.8011396674
C 0.2120873328 -2.0650130012 0.1056222407
C 1.1750336743 -1.9218938517 -0.9040891484
C 2.5348175708 -1.9619730032 -0.5430965593
C 2.9152177596 -2.0483963795 0.8225518425
C 1.9097285741 -1.8839462657 1.8119967669
C 0.5505379236 -1.8440817615 1.448693072
C -0.5879556784 -1.3738382775 2.3255936253
C 0.1248916415 1.045189485 2.5103153382
C 1.246462619 1.1931900348 1.5117784938
C 2.5195390515 1.6675636379 1.8566398028
C 3.4732948752 1.8725055844 0.8428982895
C 3.1445170033 1.5895618444 -0.4954288971
C 1.8603655855 1.1166233584 -0.7986840768
C 1.3790840942 0.8893139516 -2.2106098899
C 0.6281383055 -1.524837374 -2.256628693
C 4.3639800528 -2.2414796116 1.2135011819
O -2.2951994324 -0.9832662024 -0.5953093101
N -1.1177420078 2.8195270391 -0.4083335274
C -1.43110065 3.9406231034 -0.5287391205

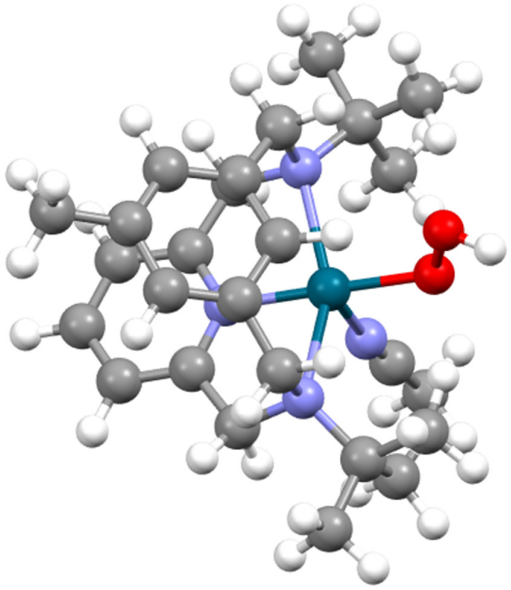
C -1.8454303307 5.3340426439 -0.6852044194
H -0.8189055564 -2.2444948718 -0.1621838034
H 3.3096443123 -1.9269423153 -1.3070254294
H 2.2048028099 -1.7890541832 2.8556128436
H -0.347289417 -1.4335953109 3.3939577659
H -1.4801443577 -1.9638631523 2.1284928148
H -0.3040158574 2.0367195876 2.6817524752
H 0.5226379572 0.699677481 3.4716751454
H 2.758406927 1.8728868628 2.894864991
H 4.4622070973 2.2441712046 1.0933431998
H 3.8701101724 1.734218038 -1.2889723361
H 2.1952806355 0.4919333587 -2.8251848699
H 1.107956222 1.8614447991 -2.6324068211
H -0.2543343115 -2.115696713 -2.49138299
H 1.3651137352 -1.6462222746 -3.0597600294
H 4.5906602913 -3.3127296721 1.3091895336
H 4.5957328248 -1.7801744217 2.1802147386
H 5.0517710812 -1.8371211798 0.4621867396
H -2.1783589598 5.5176334907 -1.7134056862
H -1.014817929 6.0125410323 -0.4598473719
H -2.6765700178 5.560750812 -0.0072903877
C -2.3498346277 0.4721163759 2.8064295083
C -2.88136325 1.8287636143 2.2901568598
C -3.4196591372 -0.6124763298 2.5318422107
C -2.0940031653 0.5572325702 4.3399095444
H -2.1633044202 2.6503351985 2.3934877531
H -3.758837663 2.1015314047 2.886347315
H -3.2006801867 1.7538621629 1.2475810722
H -3.497665656 -0.8627698152 1.4722460152
H -4.3907471321 -0.2160294456 2.8475089765
H -3.2555144169 -1.527619849 3.1095888226
H -1.6670352423 -0.3647666998 4.7491371369
H -3.0622974048 0.7029570618 4.8312968099
H -1.461268393 1.403390076 4.628158862
C -0.6321514998 0.2603304966 -3.6591127749
C -1.715267456 -0.8221665208 -3.8857813122
C -1.327090738 1.6374557798 -3.5582957308
C 0.3518703746 0.2555564402 -4.865849991
H -1.301496065 -1.7683644968 -4.2487325763
H -2.3950290655 -0.461228448 -4.6651745655
H -2.3128477023 -1.0080739791 -2.9914277781
H -2.1230345018 1.6212590377 -2.8094910479
H -1.7881005058 1.8595309929 -4.5267645366
H -0.6388969079 2.4623537609 -3.3410944858
H 1.0588078038 1.0919430522 -4.8529883105
H -0.2427168149 0.3563836864 -5.7804937556
H 0.9096108011 -0.6831595719 -4.9529240776

Int9



Pd -0.806188761 0.0055424296 0.0227908161
N 0.0329770073 1.8430034559 -0.0335097335
N -0.2183136151 0.1443233814 2.1815437763
N -0.4474837206 0.2311794514 -2.1823982757
O -1.7934144342 -1.7391824333 -0.0483626525
C 0.9733358889 -0.8428046234 -0.0297264435
C 1.647773284 -0.863109046 -1.2468985491
C 2.8875677328 -1.53584916 -1.2762277637
C 3.4237577052 -2.1270767359 -0.1055077175
C 2.7177734547 -2.004991573 1.1191840198
C 1.4702158198 -1.3535445464 1.1697444482
C 0.6234117998 -1.1296151383 2.3991174025
C 0.737546531 1.3569345577 2.2375164586
C 0.5799805839 2.3421984611 1.0986613769
C 1.0578589418 3.6625289229 1.096260548
C 0.9792075404 4.4068953444 -0.0983433506
C 0.4441034195 3.8297433334 -1.2713679787
C -0.0380506273 2.5158934498 -1.2103630193
C -0.6677004371 1.7389349006 -2.3542979285
C 1.0642714675 -0.068816339 -2.3884994264
C 4.7395931522 -2.8771242214 -0.1586335752
N -2.8735171842 0.9535328574 0.0054940805
C -4.0025258864 1.2558176687 0.0317801679
C -5.4206532722 1.6055352444 0.0720871562
H 3.4504496001 -1.5951681693 -2.2055399269
H 3.150944886 -2.4200950767 2.0266843839
H 1.2274395516 -1.0144878909 3.305389192
H -0.0706127046 -1.9592480213 2.5364436742
H 0.6361195886 1.8575743641 3.2014422945
H 1.7618959847 0.9699269436 2.1869032397
H 1.4926829885 4.0954703919 1.9911964381
H 1.3480632311 5.427861094 -0.1215060354
H 0.4084718707 4.3912526701 -2.1991378742
H -0.2512506331 2.0713437526 -3.3105250425
H -1.7447044414 1.9237582056 -2.3765549988
H 1.2041807646 -0.563469351 -3.3501203904
H 1.5841484219 0.8949151831 -2.4539438288
H 4.5705512142 -3.9459558605 -0.3491151477
H 5.2879091564 -2.7998181612 0.7862908541
H 5.3881131249 -2.5031263558 -0.9577115523
H -5.9650316456 0.893130663 0.7030968526
H -5.8524613511 1.5736904939 -0.9349305627
H -5.5603213158 2.6129890221 0.4802893856
C -1.3659845277 0.2745582971 3.2687516498
C -1.9897671598 1.6889583998 3.1864483188
C -2.4451969444 -0.8008375005 3.0178713902
C -0.7647136069 0.0651752422 4.6871768588
H -1.3502405307 2.4645702043 3.6219181069
H -2.9176715525 1.6894296502 3.7682714974
H -2.2401765424 1.9742412014 2.1624189469
H -2.9185243308 -0.6960027328 2.0406352105
H -3.2173408845 -0.694119488 3.7882315033
H -2.0581376987 -1.820125115 3.0870581717
H -0.4629440286 -0.970951534 4.8656407209
H -1.543522593 0.3018696951 5.4207119062
H 0.0861804604 0.7226549175 4.9032077157
C -1.324409114 -0.6065323459 -3.2141768193
C -0.9025292357 -2.0933350457 -3.1471569151
C -2.8221701223 -0.5000019733 -2.8553360724
C -1.1011735029 -0.0545233008 -4.6495099823
H 0.091264487 -2.2842211164 -3.5635801611
H -1.6121593096 -2.6749115726 -3.7456035417
H -0.9470732047 -2.4671682701 -2.1231963403
H -3.0399051378 -0.9713056399 -1.8952521279
H -3.3901797795 -1.0350359681 -3.6245996573
H -3.1902233197 0.5321735131 -2.8552526133
H -1.5617291734 0.9279109945 -4.8007698446
H -1.5823095171 -0.7424164623 -5.3533929394
H -0.0451648543 0.0037982678 -4.9371809494
O -1.3239647592 -2.7959052632 0.858072203
H -0.9424781994 -3.4740435936 0.2458119717

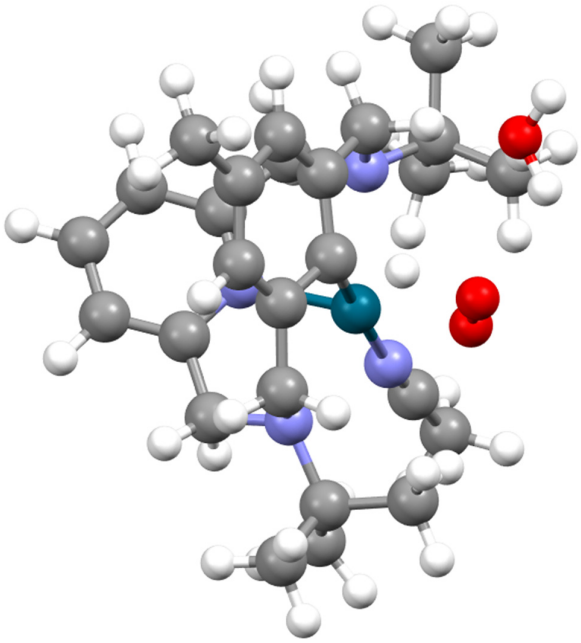
Int10



Pd -0.8226733441 0.4265294334 -0.1574992524
N 1.0231079116 1.0872311654 0.2961917725
N -0.9041191583 0.1916628813 2.2328343541
N 0.2199052072 0.1136468955 -2.2984464597
O -2.6797851403 -0.0867780747 -0.6694988069
C 0.0939130857 -1.6800357463 0.1091691485
C 1.087003813 -1.7805188781 -0.9168914304
C 2.3897714792 -2.1529389625 -0.5872732849
C 2.7599384622 -2.3953392816 0.7670464995
C 1.8151107117 -2.1033104685 1.7933699829
C 0.5088751648 -1.7321579834 1.4776752417
C -0.5030628352 -1.2691734917 2.4939239784
C 0.2292059832 1.1243750933 2.6349960641
C 1.3326261716 1.3015343699 1.6036923428
C 2.6188744757 1.749533542 1.9400535717
C 3.5612361639 1.9540801371 0.9137459015
C 3.2123111797 1.6973146348 -0.4258396795
C 1.9143959684 1.2506472405 -0.7186259723
C 1.427465723 1.0264704071 -2.1417782025
C 0.6530013668 -1.3600908029 -2.2970899604
C 4.1333781487 -2.9102359367 1.1094107198
O -2.7946853132 -1.5770430162 -0.857830801
C -2.2318913259 0.5414204053 3.0203010698
C -2.7715989431 1.9137317539 2.560620464
C -3.3215256975 -0.512473851 2.7045925325
C -1.9551419418 0.5638898705 4.5490488236
C -0.56615079 0.4493956312 -3.6352638589
C -1.6462577342 -0.6261873616 -3.9071168677
C -1.2806123001 1.8094387547 -3.485107543
C 0.4242306032 0.4943823614 -4.8329881252
H -0.9471075472 -1.9140960605 -0.1415072061
H 3.1391074574 -2.2673529048 -1.3670611976
H 2.1259860937 -2.1791789563 2.8327657616
H -0.1228522585 -1.3676801643 3.5175943284
H -1.4075223064 -1.870738891 2.4060110291
H -0.2041441441 2.1112396979 2.8208204257
H 0.6731684896 0.7929189955 3.5821158577
H 2.8795386497 1.9344869671 2.9770989672
H 4.5602713568 2.3033285216 1.1565463118
H 3.9331017821 1.8419458521 -1.2240532694
H 2.2612472135 0.6567343274 -2.7517128767
H 1.1537219019 2.0050354931 -2.5473078267
H -0.2154670922 -1.9455681709 -2.5982762916
H 1.4478972093 -1.5096862221 -3.0377026911
H 4.1221177972 -4.0110305939 1.1309342466
H 4.4658180295 -2.5780477385 2.0985526432
H 4.8828873523 -2.6162935247 0.3671076129

H -3.7342155934 -1.7450070518 -0.6030165037
H -2.0412693263 2.7274116898 2.6334999929
H -3.6108909312 2.1860136246 3.2100222423
H -3.1450221107 1.8558676077 1.5359912464
H -3.388451625 -0.6958241452 1.6287775444
H -4.288027332 -0.1147803844 3.0325997162
H -3.1812597561 -1.4583033435 3.2379464133
H -1.5392313781 -0.3804536556 4.9176599116
H -2.9073718917 0.7144797719 5.0697322773
H -1.2941472947 1.3835725823 4.8520265932
H -1.2337290801 -1.5484745037 -4.3307131051
H -2.3383546888 -0.2270066907 -4.6569730853
H -2.2282826516 -0.8620806812 -3.0131647376
H -2.107417576 1.7280995757 -2.776290792
H -1.6958379797 2.0885591892 -4.4598183358
H -0.6167793979 2.6262541601 -3.1781446922
H 1.1201097096 1.3394353652 -4.7878565497
H -0.1590776483 0.611909546 -5.7529285538
H 0.9989795885 -0.4327666741 -4.940244486
N -1.5073322363 2.5343320579 -0.351226529
C -1.9720730219 3.5962214523 -0.4968021993
C -2.5751299602 4.9134997963 -0.6880379724
H -2.9531058112 5.0116018913 -1.7123955922
H -1.8400100374 5.7062086628 -0.5088935814
H -3.4138470503 5.0512858072 0.0042547301

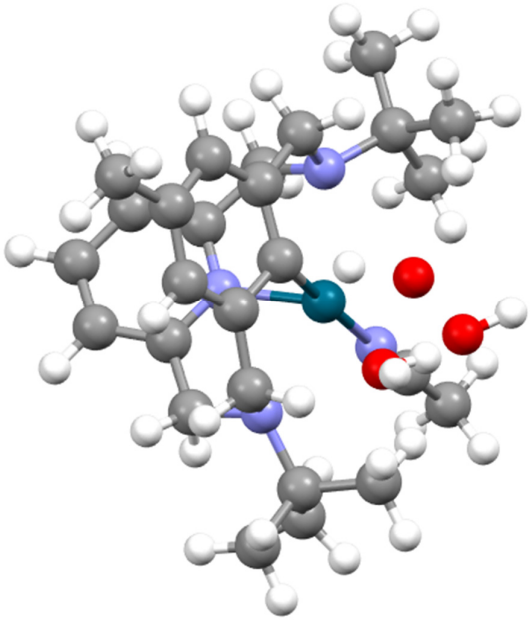
TS1



Pd 0.3082797866 5.6206604725 13.721089434
N 2.0614157211 6.4722779666 14.4058868031
N 0.0019922178 5.4380378821 16.2036756677
N 1.7104343275 5.5251802147 11.6671956732
O -1.3299346734 4.4334108963 13.0837716115
C 1.2871227763 3.8769000958 14.063263911
C 2.3276087764 3.5530432335 13.110874114
C 3.3450775572 2.6747317967 13.484102456
C 3.4383595305 2.1883311079 14.8167050638
C 2.5165647716 2.6567358791 15.7987034509
C 1.4863430048 3.527839612 15.4545625439
C 0.4908503334 4.032276866 16.4733824669
C 1.0165635602 6.4550385795 16.6541374349

C 2.2283559123 6.6181701216 15.7508112001
C 3.4779803535 6.9989473525 16.2630235659
C 4.5512725481 7.2048943329 15.3769397566
C 4.3582520446 7.0097358365 13.998235006
C 3.0906427081 6.6288910359 13.5281409315
C 2.8138087314 6.4798648798 12.0406750077
C 2.1985783859 4.0909194758 11.7099370439
C 4.5145249401 1.2069308498 15.1964644487
C -1.4080274939 5.6731846299 16.8525414088
C -1.8054246643 7.1672986088 16.7669487309
C -2.4631459456 4.8495976865 16.0789722485
C 1.0793604051 5.8643118846 10.2700860503
C -0.2525921046 5.0963036949 10.118562051
C 0.7894864024 7.3816110878 10.1542693455
C -1.389631431 5.2526739392 18.349698377
C 2.0580184297 5.4595485789 9.1314681452
C -1.5353930376 8.2873783838 13.0731537896
N -0.8206934818 7.4002423732 13.3307830722
C -2.4390695362 9.3868368301 12.7448406319
O -1.0484153609 3.0946696176 13.206363337
H 4.0916210998 2.3646185295 12.7572033425
H 2.6386654514 2.3317802831 16.82936236
H 0.9148164666 3.9615849384 17.4845358362
H -0.3785851109 3.3676606826 16.45055948
H 0.5188928618 7.4265246626 16.693868822
H 1.3652575463 6.2331315319 17.6726859467
H 3.6087091955 7.1271868144 17.3326021856
H 5.5251599241 7.4981956975 15.7567042525
H 5.1762719105 7.1458113407 13.2982413468
H 3.7499664888 6.2020246453 11.5362527231
H 2.5408455224 7.4713061275 11.6728246302
H 1.4723548363 3.4458593823 11.1962302062
H 3.1539736473 4.0010152433 11.1754083072
H 4.1338362342 0.1790369909 15.0907232376
H 4.8277420526 1.3228245635 16.2394072956
H 5.3941262506 1.2890649755 14.5501470547
H -1.3069015026 7.7900889514 17.5183988372
H -2.8799017855 7.2480134692 16.9626995834
H -1.617883528 7.5817186071 15.7725733868
H -2.5773460349 5.2076132148 15.0517466094
H -3.4299752202 4.9546997854 16.5836453056
H -2.2465882928 3.7766823718 16.0409733309
H -0.1424486299 4.0131829945 10.2214071107
H -0.6507150767 5.2840227269 9.1146036718
H -0.9971288939 5.4408813292 10.8432207756
H 0.3173817265 7.7780219463 11.0576397556
H 0.0939688277 7.5333749975 9.3220696974
H 1.6806735001 7.9766749905 9.9232052227
H -1.2754016297 4.172570199 18.4882007238
H -2.346447752 5.5314241902 18.8050962109
H -0.6028810948 5.7658297301 18.9167426109
H 3.0480836934 5.9181387501 9.2490441554
H 1.6516226654 5.8135062599 8.1773494604
H 2.1779660752 4.3751460736 9.0453082048
H -2.0164572003 10.0044166043 11.943862423
H -2.6067376785 10.0220839182 13.6222277936
H -3.4052441873 8.9927093434 12.4087680468
H 0.2400867281 3.2202727618 13.673792398
O 0.1998918249 1.755020159 10.9968735467
H 0.3072581082 0.9737079187 10.4200185998
H -0.6787465155 1.745263495 11.4278147329

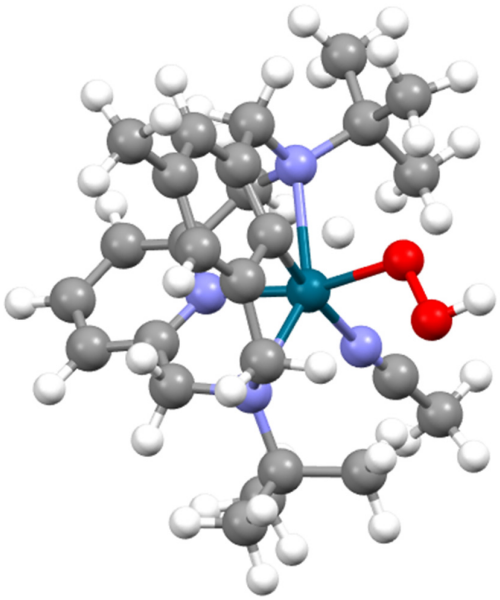
TS2



Pd -0.714569677 0.4279624826 -0.2343354467
N 1.0041377376 1.3823902517 0.407159999
N -0.9156399125 0.1976422762 2.2493045323
N 0.637862172 0.4276514066 -2.3530108945
C 0.349083236 -1.2818507503 0.0296611711
C 1.4206538531 -1.513080932 -0.9064516553
C 2.4650849407 -2.3623537128 -0.541747566
C 2.5272096335 -2.9292084471 0.7628176667
C 1.5533082546 -2.5588260752 1.7298333792
C 0.5014933581 -1.7039177516 1.3983835241
C -0.5245393151 -1.2599668295 2.4088846724
C 0.185231542 1.1018285102 2.7395252531
C 1.270689472 1.4563782314 1.7376718838
C 2.5235480778 1.9203981147 2.1768436491
C 3.4961897338 2.2793441302 1.2302500989
C 3.2086211945 2.1431793604 -0.14104752
C 1.9464040082 1.6768628705 -0.5349884605
C 1.5761041205 1.5549227334 -2.0027130646
C 1.3432974021 -0.9089770375 -2.2925746068
C 3.6316531234 -3.8882172393 1.1216382428
C -0.0227140391 0.6675325893 -3.7601332383
C -0.8476282364 -0.5733231976 -4.1867577743
C -0.9956465389 1.8656045342 -3.6824736313
C 1.0747160801 0.9407293961 -4.8271361844
H 3.2548617955 -2.5942268615 -1.2526907695
H 1.6472335756 -2.938500247 2.7440892759
H -0.157355436 -1.4396997822 3.4281042759
H -1.4054261008 -1.8976582191 2.2541376574
H -0.2624786018 2.0441149156 3.0612740744
H 0.6650619145 0.6672527463 3.6278416017
H 2.7304612556 1.9897913252 3.2400351927
H 4.4685470525 2.6388580115 1.5525214635
H 3.9537275327 2.3873540871 -0.8910889637
H 2.5044990764 1.4744770784 -2.583291675
H 1.0967668728 2.4914766038 -2.3020582268
H 0.7881506158 -1.6067751847 -2.9228312873
H 2.3521289167 -0.8294866892 -2.7230670346
H 4.5449439126 -3.6977782854 0.5483452495
H 3.3184711083 -4.9184514757 0.8919706084
H 3.8712351606 -3.8588950078 2.1894607796
H -1.5431794451 -0.270051926 -4.9770853186
H -1.4359938302 -0.9683396469 -3.3529955376
H -0.2325173009 -1.3730965911 -4.6142599433
H -1.8695178587 1.6093349847 -3.0781027401
H -1.3415758958 2.0980814442 -4.6957109426

H -0.5439951528 2.7817633624 -3.2857906839
H 1.5746895961 1.9058266992 -4.6892274462
H 0.6045650791 0.9624853007 -5.8166270732
H 1.8347512092 0.1504339994 -4.8523640187
O -1.8661005167 -1.1728044114 -1.1321135725
C -2.2748849576 0.5037849335 2.972490925
C -2.5641718312 2.0273873207 2.9622973033
C -3.4147534571 -0.2189103895 2.2264264467
C -2.2167761707 0.0183518623 4.448125938
H -2.0352501152 2.5745623402 3.7514667718
H -3.6324250402 2.1755642304 3.1523648892
H -2.3302952265 2.4819745916 1.995687046
H -3.5012509462 0.1282353735 1.1930419993
H -4.3598043474 -0.0053161144 2.7391291941
H -3.296319317 -1.3049955385 2.2105755413
H -2.1806983652 -1.0724669541 4.5295436228
H -3.126461235 0.3488324951 4.9623647919
H -1.3656356454 0.4432776032 4.9951275
H -0.7860657364 -1.6982285648 -0.4750883643
O -3.2172247734 -1.5808424415 -0.6225426128
H -3.7275676742 -1.6295402245 -1.4676032208
O -2.3747140759 -3.4055797298 1.2687072148
H -2.9049701803 -3.0173343432 0.5358316108
H -2.6325299023 -4.3254883073 1.4644048605
N -1.9589419194 2.1474377392 -0.5219379366
C -2.6884124678 3.0422558821 -0.6966904308
C -3.6085106332 4.1551558869 -0.9169177305
H -3.2449828752 5.059606439 -0.4158252521
H -4.6012932537 3.9116149005 -0.5211847385
H -3.7040816097 4.3653258643 -1.988559344

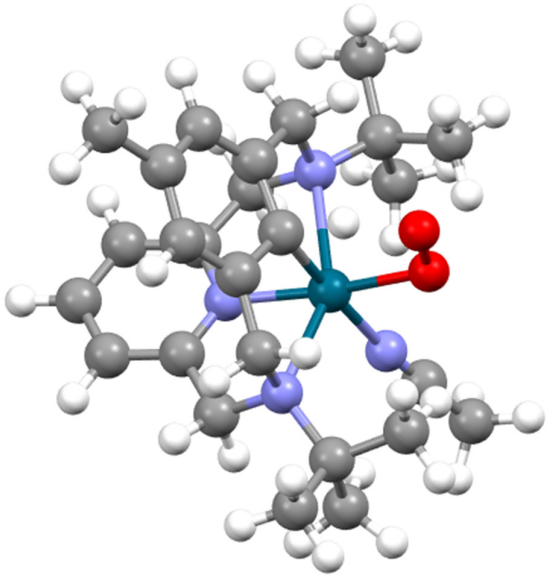
TS3



Pd -0.7505277986 0.4886486443 -0.1719858778
N 0.9912156862 1.4982582118 0.1828335449
N -0.5905251175 0.3527838243 2.316932953
N 0.4115778778 0.3193605139 -2.3644293356
O -2.1844222908 -0.9384113729 -0.7689758731
C 0.2078930887 -1.2945322502 0.0480688735
C 1.2652609429 -1.5910026896 -0.8790159543
C 2.1849186341 -2.5918779351 -0.5456866172
C 2.1435911209 -3.2345749832 0.7204588649
C 1.2155172222 -2.7806112937 1.7071261694
C 0.2871538368 -1.7893523507 1.4049054459
C -0.6352537932 -1.1630130859 2.4350232992
C 0.805154597 0.8670596276 2.5765454378
C 1.4440998056 1.6701687204 1.4525003488

C 2.5757894601 2.472460387 1.6811470244
C 3.2528531084 3.0359161576 0.5857145796
C 2.8085011035 2.7627258923 -0.7230323638
C 1.658142307 1.9821206216 -0.90423293
C 1.1016731322 1.6601467202 -2.2830144747
C 1.4032823233 -0.8118591791 -2.1785757185
C 3.0982993408 -4.3542261588 1.0401655956
C -1.6560419555 1.0744458227 3.1982719745
C -1.4780490471 2.605203862 3.0404581165
C -3.0751145019 0.6831411283 2.7319524844
C -1.4842234938 0.6808649092 4.6925193259
C -0.4322023216 0.1692726705 -3.6772489815
C -1.0235144475 -1.2601857093 -3.7640806789
C -1.6168860982 1.1620512833 -3.6507429291
C 0.4636607744 0.4401725236 -4.9172758648
H -0.9204536551 -1.580661561 -0.4191859277
H 2.962238775 -2.8770094988 -1.251240054
H 1.2604032759 -3.206471029 2.7065353744
H -0.3489116158 -1.4834048938 3.4450118842
H -1.6659225011 -1.4766436721 2.2517732739
H 0.8315230038 1.4589448644 3.4939516272
H 1.4697978232 0.0113347727 2.7577228638
H 2.9302419038 2.6337128178 2.694365021
H 4.1292019668 3.6564306764 0.7458188373
H 3.3448530486 3.1494326523 -1.5834750459
H 1.923267934 1.7207269758 -3.008963855
H 0.374438546 2.4294046195 -2.557418272
H 1.3352341851 -1.5011421312 -3.0230803206
H 2.4253370367 -0.4064900077 -2.2123246668
H 2.6122955066 -5.3233155641 0.8478340071
H 3.3923490924 -4.3534972399 2.0953470178
H 4.0004819876 -4.3183981944 0.4218597568
H -0.5787225923 2.9902242248 3.5338611518
H -2.3296569804 3.1079128238 3.5111569408
H -1.4519551338 2.8994976637 1.9873415705
H -3.2278509827 0.8887288286 1.6702938337
H -3.80400935 1.2640205516 3.3085258677
H -3.3035462064 -0.372919117 2.9014315332
H -1.731710372 -0.3704130415 4.8749973938
H -2.173202283 1.2810578246 5.2973614007
H -0.4736005118 0.8723333464 5.0741727592
H -0.2816428544 -2.0291126944 -4.0054064764
H -1.7559567138 -1.2775887018 -4.5784948422
H -1.5502567677 -1.5353492699 -2.8463205913
H -2.3039541892 0.9215113372 -2.8350365355
H -2.1673478375 1.0700889428 -4.5935028911
H -1.3077018503 2.210584263 -3.5706172179
H 0.7614101941 1.4915456692 -5.0007152551
H -0.1003148117 0.1941742348 -5.823784752
H 1.3685338576 -0.1805241913 -4.9240162912
O -3.1391768649 -1.3066451014 0.3361281762
H -3.8089275947 -1.8334165584 -0.1664563846
N -1.9630410346 2.229591658 -0.467857169
C -2.7226596419 3.0990490357 -0.6429377059
C -3.6877189424 4.173748692 -0.8606589906
H -4.5826893466 4.0074478829 -0.2498309201
H -3.9893006954 4.2080414435 -1.9139463336
H -3.254212924 5.1429597235 -0.5889708216

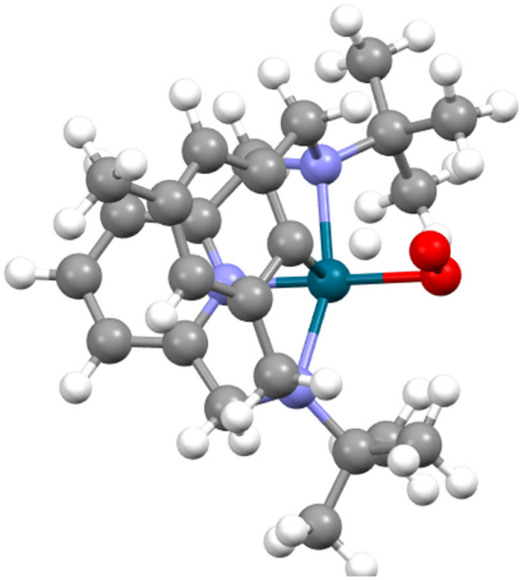
TS4



Pd 0.2244535903 5.6891474536 13.6196577968
N 2.0025744944 6.4989919077 14.2725645269
N -0.0228431114 5.4414896562 16.0999549657
N 1.5803762891 5.6157883143 11.5154433627
O -1.4425588271 4.5695127168 12.9949785927
C 1.1839582986 3.9138003674 13.8878371367
C 2.2222982852 3.6140944742 12.9224761833
C 3.2445724076 2.7309779423 13.2630893671
C 3.3445759561 2.2002011553 14.5811753194
C 2.4293844819 2.6406931292 15.5801161005
C 1.3976878446 3.5227573098 15.2667910026
C 0.4188101866 4.0098474181 16.3088267558
C 1.0394473075 6.4046635551 16.5597311773
C 2.2165403619 6.5956462683 15.6149317041
C 3.4858643181 6.955306365 16.0951596036
C 4.5271557226 7.1912665626 15.1797246432
C 4.2851402139 7.0459086953 13.8018098987
C 3.0012036314 6.6848402782 13.3638514701
C 2.6682250642 6.5902712866 11.8825665297
C 2.0984953727 4.1947138947 11.533507534
C 4.4208712636 1.2059599018 14.9211677189
C -1.4101489445 5.7038711323 16.7893644004
C -1.7559467231 7.2129951812 16.7588863694
C -2.5106586887 4.940134744 16.0174276395
C 0.9170548797 5.9503755492 10.1308444021
C -0.4021523397 5.1553010222 9.9975931965
C 0.5841546935 7.4596919497 10.0371060364
C -1.3700704984 5.2356316562 18.2716913914
C 1.8847190643 5.5846770051 8.9697410954
C -1.5908158601 8.3941650246 13.0888064727
N -0.8775184415 7.4945575353 13.3037299644
C -2.494847699 9.5082389865 12.8155759053
H 3.991249402 2.4464667671 12.5255261003
H 2.5575654257 2.2875942725 16.6005878668
H 0.8408454536 3.8822794199 17.3149262338
H -0.4721709496 3.3757536096 16.2577912808
H 0.5714023374 7.3840682648 16.6808903409
H 1.4266130171 6.1139091735 17.5465696396
H 3.6552330191 7.0450968599 17.1632890575
H 5.5146102279 7.4696521757 15.5348933706
H 5.0786068947 7.2064958893 13.0791477174
H 3.5918157775 6.3683960492 11.3294060374
H 2.3436422257 7.5848924893 11.5689238758
H 1.3921367768 3.575673097 10.9710462371
H 3.0615777918 4.1315802494 11.0088822327
H 4.0471985498 0.1836119933 14.7523693941

H 4.7193269818 1.2643754076 15.9729133059
H 5.3083282242 1.3268824921 14.291571097
H -1.2256055958 7.7929969939 17.5227951848
H -2.8238862933 7.3242378889 16.9742477989
H -1.5683552314 7.6544811627 15.7762394123
H -2.6336608457 5.3275178231 15.0021168435
H -3.4619174834 5.0676926123 16.5458939724
H -2.3367313979 3.861042274 15.9485026264
H -0.2780243642 4.071134056 10.090600527
H -0.8205922482 5.3351614172 9.0010993893
H -1.1417110921 5.4747153275 10.7372399261
H 0.1024583082 7.8283195455 10.9469217975
H -0.117088076 7.604788769 9.2085808503
H 1.4583810468 8.0816902013 9.813392089
H -1.2929082732 4.1481981175 18.3733307247
H -2.3046570192 5.5339578591 18.7596412082
H -0.551494564 5.7019960479 18.834180697
H 2.8613011284 6.0745687073 9.0708507978
H 1.4483949787 5.9317279065 8.0264935929
H 2.040528149 4.5056809376 8.8684222441
H -2.0696404648 10.1699391191 12.0520936816
H -2.6689178216 10.0939548537 13.7256369258
H -3.4583277394 9.1306961608 12.4534999763
O -1.1905334383 3.2210814083 13.0293085781
H 0.1295195873 3.3030901616 13.4934181049

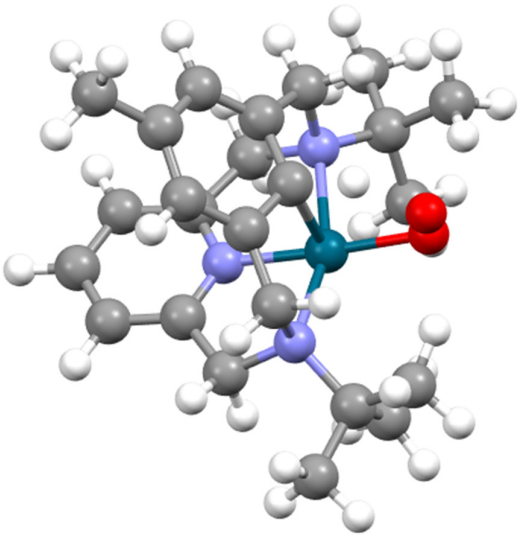
TS5



Pd 0.2714815495 5.4877393972 13.6874963767
N 1.9868195561 6.5462189138 14.1172669619
N 0.087927159 5.4710951285 15.8833518559
N 1.2075328973 5.3579603352 11.6963892497
O -1.5814923792 4.2666052278 13.2260861609
C 1.2038998429 3.6538619415 13.9864970886
C 2.1615336035 3.3966493582 12.9622432092
C 3.3032234897 2.6620399575 13.2972387196
C 3.5465544899 2.2812065386 14.6507386029
C 2.6646502782 2.7256174375 15.6808077005
C 1.5184040696 3.4609274932 15.3635823424
C 0.5267840415 4.0578305346 16.3394463048
C 1.1234593764 6.5104078678 16.3697972103
C 2.2877033479 6.7111198299 15.4287251187
C 3.5843885788 7.0965026093 15.7973525254
C 4.5488586026 7.2720556299 14.7822665143
C 4.2163313242 7.0331869325 13.4317922925
C 2.9034008685 6.6495779207 13.1238622063
C 2.3604858471 6.3865942145 11.7392228853
C 1.798047607 3.9300897603 11.5928684491
C 4.7493831693 1.4393885668 14.9955931543
C -1.3524396861 5.8829391904 16.4516252047

C -1.8363283363 7.0996389837 15.6282528746
C -2.3754585935 4.7348150552 16.2931908905
C 0.2479202755 5.7191058011 10.465368606
C -0.7328263331 4.5658107732 10.1523533964
C -0.5660625569 6.9695470034 10.8730989338
O -1.2210269273 2.9546422442 13.3579512157
C -1.2455461131 6.226601919 17.9621932226
C 1.0984957591 5.9858637052 9.1939043928
H -0.0665884781 3.058588927 13.6630120978
H 4.0248683162 2.3793804399 12.5341229304
H 2.9047528415 2.4909790985 16.7153728808
H 0.917910472 4.1091768319 17.3613457735
H -0.3692315526 3.433988944 16.3604235951
H 0.6067464207 7.4680488513 16.4667175305
H 1.4724638883 6.2311775876 17.3681983473
H 3.8418482744 7.2521378771 16.8398547193
H 5.5590067078 7.5720495631 15.0440908691
H 4.961137862 7.1399461232 12.6500125528
H 3.157087999 6.0634034065 11.0627865939
H 1.972693839 7.3309410375 11.3502187861
H 1.0249956933 3.2930853388 11.1580632021
H 2.6483189343 3.935972505 10.9022898589
H 4.4843974972 0.3717752624 14.9561871696
H 5.1151216443 1.638909654 16.0082479882
H 5.5729907178 1.5888223555 14.2896872367
H -1.1438408747 7.9492928393 15.6378499352
H -2.7791647943 7.4618493527 16.0524149821
H -2.0462760612 6.8203630905 14.5873902914
H -2.4255234224 4.3352228413 15.2795027261
H -3.3665956591 5.1442562967 16.5179430822
H -2.2170367376 3.915658484 17.0026106423
H -0.2527364449 3.7138026904 9.6594322283
H -1.4751545777 4.9485346547 9.4431655948
H -1.2858941441 4.2180427634 11.0257780443
H -1.2692670639 6.7422818626 11.6851247322
H -1.1685570327 7.294086113 10.0176937187
H 0.0501248887 7.8282839052 11.1635271445
H -0.8035909178 5.4075984766 18.5425519909
H -2.2599822493 6.3745798847 18.3482371335
H -0.6937418851 7.1481132604 18.1702731802
H 1.6921564407 6.9036422424 9.2410354957
H 0.4139851811 6.0982891679 8.3460774377
H 1.7606949888 5.1447768999 8.9552174712

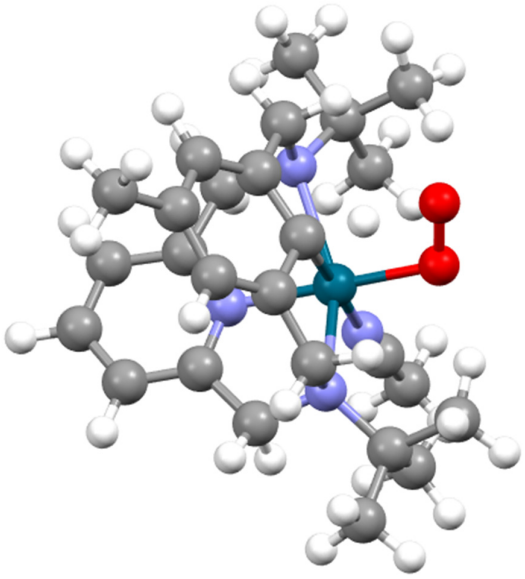
TS6



Pd 0.2610599233 5.4830098166 13.6744412012
N 2.0248409639 6.3569933188 14.1255872001
N 0.0499636448 5.4318175069 15.8939182421
N 1.2004611519 5.3216642684 11.6706345621

O -1.4506492454 4.5545348306 13.1641460132
C 1.1206611293 3.537090676 13.9441828988
C 2.1065554565 3.3480839142 12.9160953915
C 3.2971651529 2.7154476199 13.2599163768
C 3.5751677998 2.3808556928 14.6251280408
C 2.6733213544 2.7986168722 15.6526030313
C 1.4737393747 3.4347316503 15.3343650596
C 0.4693850851 4.0051308515 16.3128538847
C 1.1110927516 6.4369910465 16.3701335755
C 2.2951049526 6.5796760245 15.438544067
C 3.5756675142 7.0091319471 15.8119880055
C 4.5503429961 7.183434028 14.806219531
C 4.2387566206 6.9257410602 13.4545798535
C 2.9423018842 6.4986590419 13.1356401384
C 2.4148138065 6.2650494093 11.7373236789
C 1.6954341246 3.8596137497 11.5574677396
C 4.832645522 1.6350095996 14.9779806308
C -1.3808759372 5.8557078666 16.4699242169
C -1.8753584031 7.0271042693 15.5906044479
C -2.3876047447 4.6846040964 16.3896671567
C 0.261015603 5.7446108877 10.4435990815
C -0.7656061172 4.6331458826 10.1290447711
C -0.4883259898 7.0280434033 10.8700054409
O -1.4371200088 3.2485484588 13.6829440772
C -1.2548795481 6.278469039 17.9589638127
C 1.1274287162 5.9890341704 9.1787047567
H 0.0081095808 3.0956133798 13.7179913148
H 4.0352797438 2.4727759968 12.4991348377
H 2.9414791301 2.6192444695 16.6911571335
H 0.8526935232 4.0190758469 17.3392934299
H -0.4319167622 3.3912850107 16.2960362616
H 0.6299127096 7.416851446 16.4368876601
H 1.4402125445 6.1745189189 17.3804307258
H 3.8110199374 7.2076072377 16.8524182252
H 5.5485881155 7.5156614437 15.0751230951
H 4.9848258586 7.0591513888 12.6780925239
H 3.2050949404 5.8909776459 11.0789863863
H 2.1026444257 7.2342037473 11.3397185544
H 0.8529745046 3.2657683805 11.1949426666
H 2.4992270148 3.8005220469 10.8159832066
H 4.6411865028 0.5500941429 14.9444957856
H 5.1803843462 1.8620085719 15.9910107165
H 5.6448685395 1.8318637851 14.2702668727
H -1.1687942334 7.8656384688 15.5383733165
H -2.8020462585 7.4289853866 16.0152966268
H -2.1168075855 6.682379624 14.5769663969
H -2.3821720786 4.1625763897 15.430698856
H -3.3929536724 5.1002001951 16.5216690018
H -2.2456692708 3.9589638965 17.1987674026
H -0.3276755028 3.7951001896 9.5761905315
H -1.5336325351 5.0634963817 9.4764069551
H -1.2786080254 4.2689764213 11.0227021246
H -1.2225593054 6.818579431 11.6574617962
H -1.0499530454 7.411608101 10.0110910765
H 0.1730409592 7.8406983587 11.195758755
H -0.7824043303 5.500441497 18.5716159552
H -2.266331152 6.4192329493 18.3550722779
H -0.7241437485 7.2237920706 18.1105366402
H 1.7593572519 6.8808509746 9.2378253649
H 0.4492532659 6.1400519948 8.3317859318
H 1.753234598 5.1233521112 8.9296263402

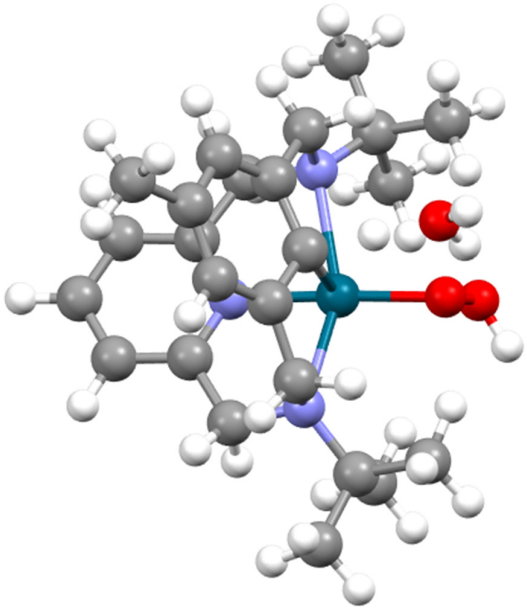
TS7



Pd 0.1809715826 5.6363037902 13.721442925
N 2.0577517004 6.3391975998 14.1329714762
N 0.0866986209 5.5054659356 16.0448553557
N 1.2186747204 5.3285493105 11.5453722475
O -1.6096301213 4.788705207 13.4209760955
C 1.021801473 3.6933913621 13.9771347602
C 2.0024259701 3.4165621213 12.9489293165
C 3.1723831323 2.7358587321 13.2739650101
C 3.4626224023 2.3766129344 14.6221408566
C 2.5870178717 2.820722215 15.6581492724
C 1.4118886637 3.4986353022 15.3561409022
C 0.4670726338 4.0551414497 16.3778955128
C 1.2271224672 6.4461430857 16.4368858868
C 2.371656285 6.5345926381 15.4379260476
C 3.6854358095 6.883153019 15.783834028
C 4.6447260432 7.0052492044 14.7571992092
C 4.2841191878 6.7701118065 13.4155166115
C 2.9548112975 6.4239401329 13.1215670134
C 2.4347338751 6.2335777446 11.7035907465
C 1.6447498764 3.8614515959 11.5602287684
C 4.6889360106 1.5712559036 14.9530402788
C -1.2541015421 5.8898670837 16.8244702536
C -1.8035381444 7.2350055145 16.3061696105
C -2.3373518262 4.8094513069 16.5834994833
C 0.4604118713 5.6545228755 10.1866911445
C -0.6154500221 4.5799973727 9.8961580647
C -0.2491885489 7.0205362661 10.2982190742
C -0.952332599 5.9944451055 18.3460944931
C 1.4784885129 5.6833384822 9.0095542906
C -1.0437928273 8.6793690702 13.2285299876
N -0.5670871739 7.6319132686 13.4214614789
C -1.6638751197 9.9774624574 12.977719709
H 3.8820986469 2.4689620847 12.494672332
H 2.8555587354 2.6234027453 16.6931746059
H 0.8794495159 4.0049722334 17.3919823939
H -0.4541381418 3.469950594 16.3600794311
H 0.8009179278 7.4479177054 16.5426292941
H 1.6201900964 6.1600770203 17.4188427047
H 3.9574715761 7.0542017314 16.8203802441
H 5.6677515736 7.2737940803 15.0029232223
H 5.0190849449 6.8543042979 12.6214499124
H 3.2532575387 5.8723509771 11.0693606717
H 2.1564420069 7.2220630868 11.3260188516
H 0.7880897233 3.2773060475 11.2209221402
H 2.4688214552 3.6994020804 10.8544588254
H 4.4375400712 0.4986000976 14.9565712262
H 5.0819009725 1.8055400795 15.9480742848
H 5.4856718158 1.70687585 14.2145549144

H -1.0648918034 8.0443890739 16.2953390903
H -2.6094499801 7.5522767998 16.9768652795
H -2.2304132931 7.1186015056 15.3079330159
H -2.3980440565 4.5207990531 15.5298934527
H -3.3083562233 5.2358850168 16.8589451875
H -2.2080680049 3.9207050428 17.2102329097
H -0.1971504825 3.6678072065 9.4562470988
H -1.3115795944 4.9866611489 9.1542429141
H -1.1962082204 4.3150341637 10.784831446
H -1.1130239961 6.9497740517 10.9631856981
H -0.6144065484 7.2986784505 9.3036017114
H 0.403942975 7.8339238601 10.6353516334
H -0.5019664499 5.0829944546 18.7545815297
H -1.9050745031 6.1343892064 18.8686008374
H -0.3195040809 6.8509605814 18.6025892932
H 2.1658156342 6.5352579056 9.0532753231
H 0.9137280451 5.7766461014 8.0755355849
H 2.0622802336 4.7588773844 8.9328621589
H -0.9517112799 10.7899962665 13.1610808339
H -2.531031257 10.1167903474 13.634012098
H -2.0053976383 10.0389470391 11.9376230612
O -1.3798749501 3.5331953747 12.8568193818
H -0.0233600671 3.2580753593 13.6812944952

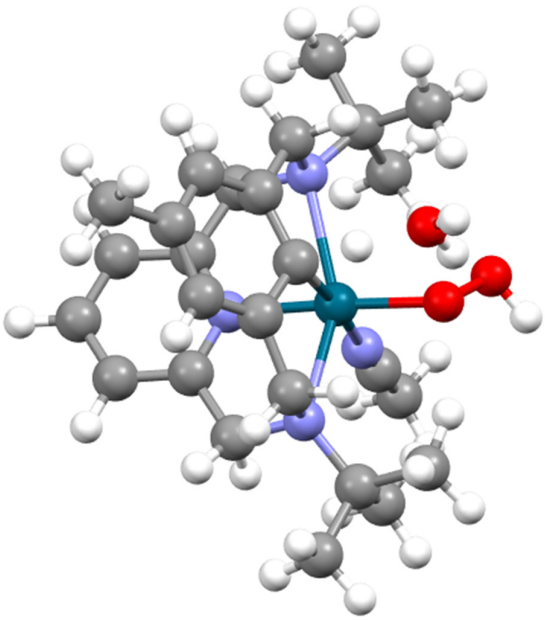
TS8



Pd -0.8465774394 0.2007820525 -0.1016895524
N 0.8932142517 1.1776098612 0.2992102732
N -0.8721210541 0.1323082749 2.311588033
N 0.2577782434 0.1316873268 -2.2993517695
C 0.2833810257 -1.5344585975 0.1554032286
C 1.2721353947 -1.695776052 -0.8718278344
C 2.4753142666 -2.3312050057 -0.5514390555
C 2.7644576577 -2.7059610945 0.7921769114
C 1.8462971521 -2.364352433 1.8292572522
C 0.6374722172 -1.732078842 1.5310918117
C -0.355450595 -1.2718712021 2.5858089138
C 0.1776641323 1.1552324041 2.6722686595
C 1.219389458 1.4211892333 1.6037044823
C 2.4604282522 1.9896495532 1.925584801
C 3.3667161573 2.2956021011 0.8947694548
C 3.0171374456 2.0162601977 -0.4379832559
C 1.7663283127 1.4453380933 -0.7164130011
C 1.3119571989 1.1979327809 -2.1390766603
C 0.9052372565 -1.2441182841 -2.2740301878
C 4.0468734883 -3.4253931034 1.1213963605
C -2.2325380136 0.4497322681 3.0249983999

C -2.8109243511 1.7386471819 2.392207495
C -3.2384547468 -0.706010693 2.8047122178
C -2.0176636457 0.6421334232 4.5509455847
C -0.594370912 0.3820408166 -3.597016437
C -1.6078510434 -0.7692405964 -3.7971533225
C -1.381206978 1.7043851626 -3.4259386495
C 0.333249632 0.4649200592 -4.8401940672
H -0.7031183796 -2.4093434465 -0.2170979891
H 3.2130330501 -2.5325777554 -1.325041193
H 2.1121645967 -2.585460383 2.8606206636
H 0.0885560343 -1.3282818981 3.5888454687
H -1.2157938039 -1.9446796834 2.5691496548
H -0.3248526111 2.105331732 2.8725147794
H 0.6842507193 0.8712828141 3.604119134
H 2.7106158148 2.1909649363 2.9621807267
H 4.3306230816 2.7379842543 1.1269027711
H 3.7022696319 2.2377438159 -1.2497827619
H 2.1892989554 0.9670271466 -2.7576910391
H 0.9040010101 2.1392627125 -2.5165258859
H 0.1795117128 -1.953994669 -2.6780481032
H 1.7868676825 -1.2645552203 -2.9286529073
H 3.8885655486 -4.5138351159 1.0724402802
H 4.3966239513 -3.2009999771 2.1344134772
H 4.8460449757 -3.1883367265 0.4116585424
H -2.1867269747 2.6260011394 2.5465750185
H -3.7808044401 1.9602845694 2.8504850418
H -2.9731044779 1.6140017025 1.3142695084
H -3.278911291 -1.0156877095 1.7566505498
H -4.2355739474 -0.3542478346 3.0914915058
H -3.0299621183 -1.5759877339 3.4375332184
H -1.5563598809 -0.2383993654 5.0145998727
H -2.993114493 0.7814056333 5.030257669
H -1.4154349563 1.5237336243 4.7952959617
H -1.1410356268 -1.7012786159 -4.1351710964
H -2.3087271938 -0.4747959857 -4.5853539459
H -2.1956028258 -0.9542043377 -2.8962194449
H -2.0247665083 1.6720006071 -2.5417824168
H -2.0331181944 1.8377655744 -4.296066165
H -0.7450545438 2.5959323937 -3.3839407248
H 1.014614594 1.3223229799 -4.8092824515
H -0.2884852201 0.5861968258 -5.7341756388
H 0.9221673406 -0.4492448906 -4.9822706624
O -2.5979897885 -0.7628416758 -0.4239966068
O -1.6887584745 -3.0002136753 -0.6938283898
H -2.391749472 -2.2689025323 -0.8078763928
H -1.957829953 -3.9327438162 -0.6099724173
O -3.3775790384 0.281131635 -1.1463831604
H -4.1667722499 0.4101710644 -0.5609435377

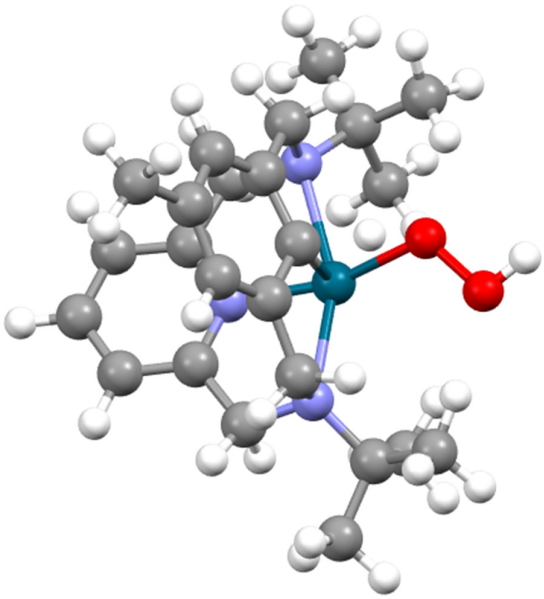
TS9



Pd -0.8888332765 0.3597845739 -0.0903595619
N 0.9617609649 1.1871201535 0.1935929213
N -0.7299715932 0.2913890909 2.4164214365
N 0.1494817197 0.0703916823 -2.3956466445
C 0.1867222501 -1.4205213069 0.1734102872
C 1.1211775859 -1.6957728107 -0.8961120675
C 2.3229362169 -2.3524040973 -0.6300366765
C 2.6944304763 -2.6825570592 0.7020735864
C 1.8586884923 -2.2613579948 1.7750522664
C 0.6527162764 -1.6072149087 1.5288642379
C -0.2316951407 -1.1168765961 2.6507785431
C 0.3778167467 1.2899045981 2.6177429504
C 1.3664740932 1.4477102248 1.4689924373
C 2.6610247515 1.9385769822 1.7022376762
C 3.5269186439 2.1445941797 0.6136235983
C 3.0875983047 1.8434829924 -0.6874652035
C 1.7857664844 1.3529184376 -0.8786985633
C 1.2514313963 1.0879052871 -2.2790064312
C 0.700505132 -1.3329627785 -2.2989726525
C 3.9640663707 -3.4438525862 0.9765796666
C -1.9796948487 0.6174101888 3.3035966782
C -2.6269471874 1.9394446253 2.8317867605
C -3.0420354396 -0.4993296558 3.1462769972
C -1.564275415 0.7337003313 4.7966504001
C -0.6832385883 0.2751787962 -3.7103211014
C -1.6954314299 -0.883338322 -3.8852094278
C -1.4879049674 1.5911798435 -3.6136368019
C 0.2635297461 0.3169408195 -4.9432772606
H -0.7749223493 -2.2036844169 -0.0497095789
H 2.9946073711 -2.6143304064 -1.4442441876
H 2.1812516541 -2.4487958506 2.7966756783
H 0.2918005172 -1.1864956509 3.6148300318
H -1.1051666546 -1.7703837059 2.7058110468
H -0.079463474 2.2697892555 2.782275837
H 0.9467645143 1.0554028683 3.5285149961
H 2.9840494988 2.1529101046 2.7159044945
H 4.5309601766 2.5236684895 0.7778576014
H 3.7435731792 1.9829783168 -1.5406386034
H 2.0998899311 0.8111831112 -2.9205910231
H 0.8695386801 2.0387156088 -2.6626018348
H -0.0971333153 -2.0204230245 -2.5896368673
H 1.5332437544 -1.4720199568 -3.0031984047
H 3.7541921828 -4.5246433705 0.9906115906
H 4.3928413162 -3.1914245273 1.9519949174
H 4.7201433618 -3.2769498763 0.2025815363
H -1.9409654492 2.7942471889 2.8261717658

H -3.4387666063 2.193784162 3.5220568362
H -3.055195894 1.8212607241 1.8336559989
H -3.2001607852 -0.7502635727 2.0923480905
H -3.9926693412 -0.1311864465 3.5478533376
H -2.8029984354 -1.405642152 3.7135710632
H -1.0655599348 -0.1716146697 5.162300085
H -2.4653737705 0.8688015138 5.4052829926
H -0.9146685982 1.5948387416 4.9909277402
H -1.2313201278 -1.8104334246 -4.2395016089
H -2.4214583042 -0.5903193281 -4.6514918638
H -2.2574850991 -1.0747494853 -2.967998169
H -2.2590076473 1.5065010653 -2.8452390539
H -1.983271313 1.7650742193 -4.5754535451
H -0.8669617649 2.4738652825 -3.4175348384
H 0.9073521069 1.2037411304 -4.9575320214
H -0.3470712153 0.3513321032 -5.8523556168
H 0.8941041387 -0.5772698456 -5.0171456815
O -2.7249255947 -0.5531819633 -0.2252638847
O -1.9092310845 -2.8670760028 -0.4600660546
H -2.5491083044 -2.0672100518 -0.47325602
H -2.2644400733 -3.7562952001 -0.2842032222
O -3.5628045369 0.0735575618 -1.2950193098
H -4.3709688347 0.3338046306 -0.7880492029
N -1.7362253539 2.3225939721 -0.3513397927
C -2.2166677883 3.3699697253 -0.5353011973
C -2.8349110227 4.6716691915 -0.7775400771
H -3.3392885037 4.6757361218 -1.7508535381
H -2.0791115226 5.4652283154 -0.773024439
H -3.5763234489 4.8935238332 -0.001203054

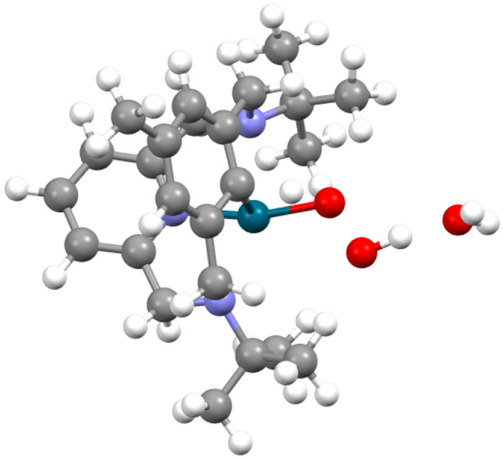
TS10



Pd -0.6111948215 0.4117799805 -0.1678698834
N 1.179210127 1.2993954838 0.212564341
N -0.6485134681 0.4301777716 2.2810128524
N 0.4146860524 0.2068349242 -2.3369855503
O -2.02694394 -1.0451384911 -0.7230376494
C 0.2824438747 -1.3908893289 0.1389573872
C 1.175636964 -1.7557530338 -0.9278322855
C 2.2173587559 -2.6336224983 -0.62968955
C 2.4570408333 -3.0535143237 0.7135198087
C 1.6708372026 -2.513313043 1.7742782124
C 0.6188052784 -1.633283798 1.5130756103
C -0.216140609 -0.9856848276 2.6086191751
C 0.4543360951 1.422247043 2.5647814731
C 1.5338563715 1.5271905109 1.5094695508
C 2.8394928103 1.9376845748 1.8166039122

C 3.7743267836 2.092689537 0.7765939499
C 3.3904294382 1.8178977094 -0.5489059083
C 2.0751534929 1.4077344567 -0.8115487698
C 1.5798139947 1.1596512217 -2.2226928499
C 0.8855921052 -1.235687602 -2.3288719237
C 3.5616791636 -4.0307038167 1.0129828007
C -1.9767129214 0.8920554456 3.0032511911
C -2.5955599018 1.9956658316 2.114372454
C -2.9824159153 -0.2724214611 3.1451472644
C -1.6756289812 1.4249051859 4.4335947014
C -0.5040986123 0.58793042 -3.55553277
C -1.5264548528 -0.5347478745 -3.850426198
C -1.2787962977 1.8681144699 -3.1605094841
C 0.3529684723 0.8206996889 -4.8295266675
H 2.8736071834 -2.9941459346 -1.4183421092
H 1.9181978286 -2.7806257796 2.7988982203
H 0.3253918753 -1.0166493449 3.5648290735
H -1.1221269482 -1.583415983 2.7342597193
H -0.0035276239 2.4126695734 2.646231985
H 0.9192462205 1.2129528332 3.5366193869
H 3.1175637292 2.1320290375 2.8472789278
H 4.7887327549 2.4109285933 0.9966348747
H 4.0992726683 1.9184387877 -1.3643986785
H 2.417340818 0.8176247854 -2.8441438331
H 1.2689895379 2.1263856091 -2.6285868054
H 0.0864765334 -1.8457952351 -2.7571225987
H 1.7677581518 -1.3596324153 -2.9716576128
H 3.1701660924 -5.059104683 0.9616842313
H 3.9705686476 -3.8971886757 2.0196236984
H 4.3782997868 -3.9666953574 0.2865166971
H -1.9017023044 2.8207514869 1.9058159805
H -3.462411227 2.4354342231 2.6202889121
H -2.9534332105 1.5726193732 1.1666508899
H -3.1347302211 -0.8171070754 2.2121188092
H -3.9506650546 0.155498045 3.4284759017
H -2.707511112 -0.9679838403 3.9470223338
H -1.1150976398 0.6952139574 5.0320889892
H -2.6294285318 1.5903232019 4.945939212
H -1.1418783304 2.3805954125 4.4498973089
H -1.0823148144 -1.3837951563 -4.3825030415
H -2.2968609348 -0.1269984361 -4.5140132046
H -2.0266711639 -0.8863550587 -2.9438106593
H -1.9769663637 1.6652153943 -2.3364034174
H -1.8796469889 2.2066087646 -4.0117316969
H -0.6314904075 2.7083751162 -2.88203504
H 0.9894589496 1.7101190863 -4.7730227289
H -0.3187507285 0.9663995023 -5.6826236826
H 0.9813210186 -0.0484089899 -5.061921737
H -0.9688295624 -1.6847837648 -0.196967161
O -3.2488444701 -1.1366847485 0.1328716114
H -3.852102653 -1.6668824616 -0.4480809508

TS11



Pd -0.622940793 0.2146518534 -0.137903309
N 1.0025736533 1.3683409597 0.24709173
N -0.7330800616 0.3098999916 2.302588278
N 0.4692814707 0.0804054761 -2.2647705066
C 0.5088574276 -1.454122124 0.2614085597
C 1.4755817256 -1.6998742931 -0.7685093143
C 2.6569489924 -2.3534560082 -0.4143556759
C 2.9391903903 -2.6592549888 0.9500414473
C 2.0432550735 -2.2228691213 1.9686842957
C 0.851206462 -1.5677795574 1.6458169184
C -0.1068890572 -1.0173047086 2.6938771499
C 0.2037610345 1.4637254772 2.5741117985
C 1.2856231697 1.6899513318 1.5414683966
C 2.5110126963 2.292274066 1.8624890392
C 3.4441049995 2.5403799754 0.8393335012
C 3.1417730577 2.1635840525 -0.4820228791
C 1.9052203884 1.5620562427 -0.7581869135
C 1.4936201921 1.1862388133 -2.1676771868
C 1.1314351802 -1.2865901079 -2.1936219872
C 4.1997870601 -3.3995322573 1.3146637187
C -0.4592705914 0.2871428236 -3.5163911841
C -1.320073672 -0.9708456688 -3.781626539
C -1.4052415727 1.4693758975 -3.1953895706
C 0.392483828 0.578031438 -4.7820927377
H 3.387336394 -2.6183361685 -1.1754829307
H 2.3122447499 -2.3863144942 3.0097209931
H 0.401440849 -0.9340283489 3.6651096124
H -0.9207452084 -1.7351077731 2.8152761235
H -0.3973318072 2.3775292569 2.6057165607
H 0.6660929813 1.3595006594 3.56395166
H 2.7296518891 2.5598433342 2.8910234589
H 4.3967214628 3.0073313449 1.0698934595
H 3.8537529067 2.3306508904 -1.2837149002
H 2.3887273177 0.9312592939 -2.7494281687
H 1.0706796679 2.0829806871 -2.629038335
H 0.4237104938 -2.013217582 -2.5986833604
H 2.0281300881 -1.3135762852 -2.8274209361
H 5.0078528895 -3.2149714918 0.599168342
H 4.0097766753 -4.4840960519 1.3086744825
H 4.552552122 -3.1439166325 2.3190303009
H -2.1186171934 -0.6930154095 -4.4785519515
H -1.7924437844 -1.3475681182 -2.8702398818
H -0.7552328522 -1.7751130205 -4.2668978057
H -2.0948806897 1.2082336535 -2.3811091152
H -2.0173514861 1.6941192475 -4.0758077722
H -0.8808833822 2.3964386279 -2.9344213068
H 0.9058250762 1.5450258019 -4.7521707278
H -0.2701508754 0.5984452215 -5.6543337885
H 1.1351384052 -0.209448833 -4.9622689784
O -1.8111053196 -1.4096994951 -0.6598665989
C -2.1301560546 0.5947544925 2.9861693604
C -2.8882159346 1.5584072954 2.0441181619
C -2.9542113253 -0.7009179058 3.1588835822
C -1.9424505688 1.2195475238 4.3988157972
H -2.3173210347 2.4663473361 1.8078644966
H -3.8178635107 1.8874957287 2.5221561339
H -3.1619425941 1.0460682928 1.1133598318
H -2.9981038612 -1.291482675 2.2420692561
H -3.9820006396 -0.4115498479 3.406329178
H -2.5968422696 -1.3154244909 3.9939104082
H -1.2904678087 0.6059438004 5.0339335068
H -2.9210765079 1.255947306 4.8893608829
H -1.5603459371 2.2454198041 4.3860891055
H -0.7006471632 -1.8924220116 -0.0991540993
O -3.017710309 -1.6093641897 0.1806125431
H -3.5593222615 -2.3148226167 -0.3587374625
O -4.4637176613 -3.2963696644 -1.053827759
H -4.4710772392 -4.2576027897 -0.888827607
H -5.242715743 -3.0149432661 -1.5691697821

10. References

1. Ruhs, N. P.; Khusnutdinova, J.; Rath, N. P.; Mirica, L. M., Mononuclear Organometallic Pd(II), Pd(III), and Pd(IV) Complexes Stabilized by a Pyridinophane Ligand with a C-Donor Group. *Organometallics* **2019,** *38* (19), 3834-3843.
2. Zhou, W.; Schultz, J. W.; Rath, N. P.; Mirica, L. M., Aromatic Methoxylation and Hydroxylation by Organometallic High-Valent Nickel Complexes. *J. Am. Chem. Soc.* **2015,** *137* (24), 7604-7607.
3. Achord, J. M.; Hussey, C. L., Determination of dissolved oxygen in nonaqueous electrochemical solvents. *Anal. Chem.* **1980,** *52* (3), 601-602.
4. Franco, C.; Olmsted, J., Photochemical determination of the solubility of oxygen in various media. *Talanta* **1990,** *37* (9), 905-909.
5. Casado, J.; Lopezquintela, M. A.; Lorenzobarral, F. M., The Initial Rate Method in Chemical-Kinetics - Evaluation and Experimental Illustration. *J. Chem. Educ.* **1986,** *63* (5), 450-452.
6. Xing, W.; Yin, M.; Lv, Q.; Hu, Y.; Liu, C. P.; Zhang, J. J., Oxygen Solubility, Diffusion Coefficient, and Solution Viscosity. *Rotating Electrode Methods and Oxygen Reduction Electrocatalysts* **2014**, 1-31.
7. Li, Q.; Batchelor-McAuley, C.; Lawrence, N. S.; Hartshorne, R. S.; Compton, R. G., Anomalous solubility of oxygen in acetonitrile/water mixture containing tetra-
-butylammonium perchlorate supporting electrolyte; the solubility and diffusion coefficient of oxygen in anhydrous acetonitrile and aqueous mixtures. *J. Electroanal. Chem.* **2013,** *688*, 328-335.
8. Horstmann, S.; Grybat, A.; Kato, R., Experimental determination and prediction of gas solubility data for oxygen in acetonitrile. *J. Chem. Thermodyn.* **2004,** *36* (11), 1015-1018.
9. Lee, Y.; Park, G. Y.; Lucas, H. R.; Vajda, P. L.; Kamaraj, K.; Vance, M. A.; Milligan, A. E.; Woertink, J. S.; Siegler, M. A.; Sarjeant, A. A. N.; Zakharov, L. N.; Rheingold, A. L.; Solomon, E. I.; Karlin, K. D., Copper(I)/O
Chemistry with Imidazole Containing Tripodal Tetradentate Ligands Leading to μ-1,2-Peroxo-Dicopper(II) Species. *Inorg. Chem.* **2009,** *48* (23), 11297-11309.
10. Ananikov, V. P., Nickel: The "Spirited Horse" of Transition Metal Catalysis. *ACS Catal.* **2015,** *5* (3), 1964-1971.
11. Eisenberg, G. M., Colorimetric determination of hydrogen peroxide. *Ind. Eng. Chem. Anal. Ed.* **1943,** *15*, 327-328.
12. Qu, F.; Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M., Dioxygen activation by an organometallic Pd(II) precursor: formation of a Pd(IV)-OH complex and its C-O bond formation reactivity. *Chem. Commun.* **2014,** *50* (23), 3036-3039.
13. Bruker, APEXIII. Bruker AXS, Inc. *Madison, Wisconsin, USA* **2018**.
14. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D., Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **2015,** *48*, 3-10.
15. Sheldrick, G. M., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A* **2015,** *71* (1), 3-8.
16. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42* (2), 339-341.
17. Sheldrick, G. M., Bruker-SHELXTL. *Acta Cryst. A* **2008,** *64*, 112-122.
18. Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J.

V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J., Gaussian 16, Revision C.01. *Gaussian, Inc., Wallingford CT* **2016**.

19. Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H., Energy-Adjusted Abinitio Pseudopotentials for the 2nd and 3rd Row Transition-Elements. *Theor. Chim. Acta* **1990,** *77* (2), 123-141.
20. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009,** *113* (18), 6378-6396.