Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Dioxygen Activation by an Organometallic Pd(II) Precursor: Formation of a Pd(IV)-OH Complex and Its C-O Bond Formation Reactivity

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I. General specifications

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk and glove box techniques if not indicated otherwise. All reagents for which synthesis is not given were commercially available 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. ^{1}H (300.121 MHz) NMR spectra were recorded on a Varian Mercury-300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. Abbreviations for the multiplicity of NMR signals are s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). UV-visible spectra were recorded on a Varian Cary 50 Bio spectrophotometer and are reported as λ_{max}, nm (ε, M^{-1} cm^{-1}). EPR spectra were recorded on a JEOL JES-FA X-band (9.2 GHz) EPR spectrometer in MeCN glass at 77 K. ESI-MS experiments were performed using a Bruker Maxis QTOF mass spectrometer with an electrospray ionization source. ESI mass-spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954). Cyclic voltammograms were recorded using a BASi EC Epsilon electrochemical workstation or a CHI 660D Electrochemical Analyzer and a glassy carbon working electrode (GCE), a platinum-wire auxiliary electrode, and a Ag/0.01 M $AgNO_3$/MeCN reference electrode. Electrochemical grade Bu_4NClO_4 (tetrabutylammonium perchlorate, TBAP) or Bu_4NPF_6 from Fluka were used as the supporting electrolytes at a concentration of 0.1 M in nonaqueous solutions. Potentials are reported relative to Fc^+/Fc in TBAP/MeCN or Bu_4NPF_6/MeCN. The analyzed solutions were deaerated by purging with nitrogen for 10 min.

II. Synthesis of (Me_3tacn)Pd complexes

Preparation of (COD)Pd($CH_2CMe_2C_6H_5$)Cl.

The compound (COD)Pd($CH_2CMe_2C_6H_5$)Cl was prepared according to the literature reported procedure.[1] To the 0.50 g (COD)$PdCl_2$ in 50 mL of dry Et_2O at -70 °C, Mg($CH_2CMe_2C_6H_5$)Cl (0.5 M in Et_2O, 4.0 mL , 1.0 eq) was added. The solution was stirred at low temperature for 30 min, then it was allowed to reach RT and stirred overnight. The resultant dark suspension was filtered. The residue was washed with Et_2O. The light yellow filtrates were combined, evaporated to dryness. The pale yellow product was re-dissolved in ~ 80 mL of Et_2O. The solution was concentrated to ~ 10 mL, with large amount of white microcrystalline precipitate. The precipitate was collected by suction filtration, dried to give pale yellow to white product. Yield: 0.3328 g, 0.8427 mmol, 48.2%.

Preparation of (COD)Pd($CH_2CMe_2C_6H_4$).

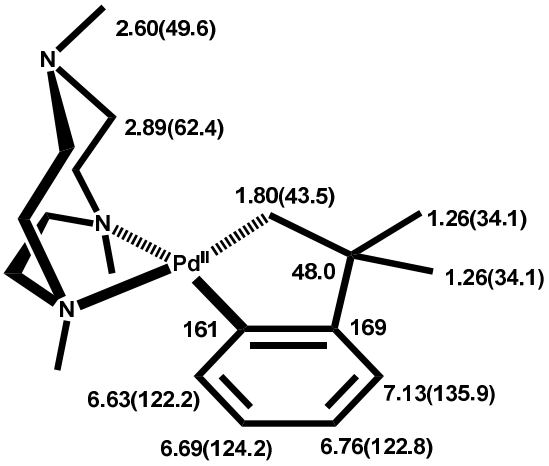
The compound (COD)Pd($CH_2CMe_2C_6H_4$) was prepared according to the literature reported procedure.[2] (COD)Pd($CH_2CMe_2C_6H_5$)Cl (0.20 g, 0.52 mmol) in THF, NaOH (0.063 g, 1.57 mmol, 3 eq) and H_2O (0.16 mL) were added. The solution was stirred under N_2 at RT in the dark for 3 h. The solution was concentrated to dryness, followed by extraction with ether and filtered. The filtrate was concentrated until some brown precipitate formed. Then some petroleum ether was added. The mixture was left in -20 °C freezer overnight. The crystals were collected by suction filtration, dried to give light brownish crystals. Yield: 110 mg, 0.317 mmol, 61%.

Preparation of Me_3tacnPd^{II}($CH_2CMe_2C_6H_4$) (1).

Inside the glovebox, (COD)Pd($CH_2CMe_2C_6H_4$) (300 mg, 0.865 mmol) was dissolved in 20 mL of dry diethyl ether, followed by addition of Me_3tacn (175 mg, 1.038 mmol) in 5 mL of ether while stirring. The reaction mixture was stirred at RT overnight. The resulting colorless solution was filtered, evaporated to dryness and triturated with small amount of pentane. The white solid was collected by filtration, washed with 1 mL of pentane, dried under vacuum. Yield: 287 mg, 0.700 mmol, 81%.

^{1}H NMR (600 MHz, CD_3CN), δ: 7.13 (d, *J* = 7.4 Hz, 1H, Ph-H), 6.76 (t, *J* = 7.4 Hz, 1H, Ph-H), 6.69(t, *J* = 7.4 Hz, 1H, Ph-H),6.64 (d, *J* = 7.4 Hz, 1H, Ph-H), 3.05-3.95 (br m, 6H, CH_2), 2.73-3.00 (br m, 6H, NCH_2), 2.60 (s, 9H, NCH_3),1.80 (br s, 2H, $PdCH_2$), 1.26 (s, 6H, CMe_2). ^{13}C NMR (151 MHz, CD_3CN), δ: 169.0 (Ph), 161.2, 135.9, 122.8, 124.1, 122.1, 62.4(N*C*H_2), 49.6

(br, N*C*H$_3$), 48.0 (*C*Me$_2$), 43.4 (Pd*C*H$_2$), 34.0 (br, C*Me$_2$*). Anal. Found: C, 55.89; H, 8.35; N, 10.19. Calcd for $C_{19}H_{33}N_3Pd$: C, 55.67; H, 8.11; N, 10.25.



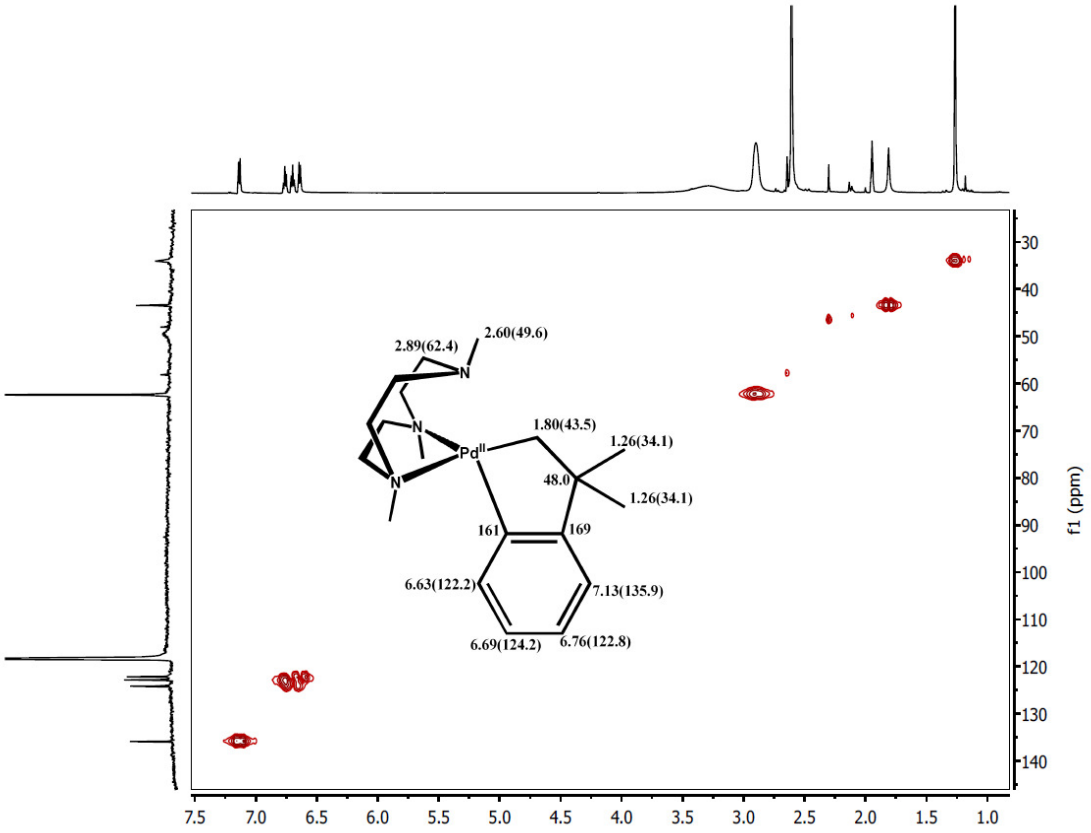


Figure S1. ^{1}H-^{13}C HMQC spectrum of compound **1** in CD_3CN.

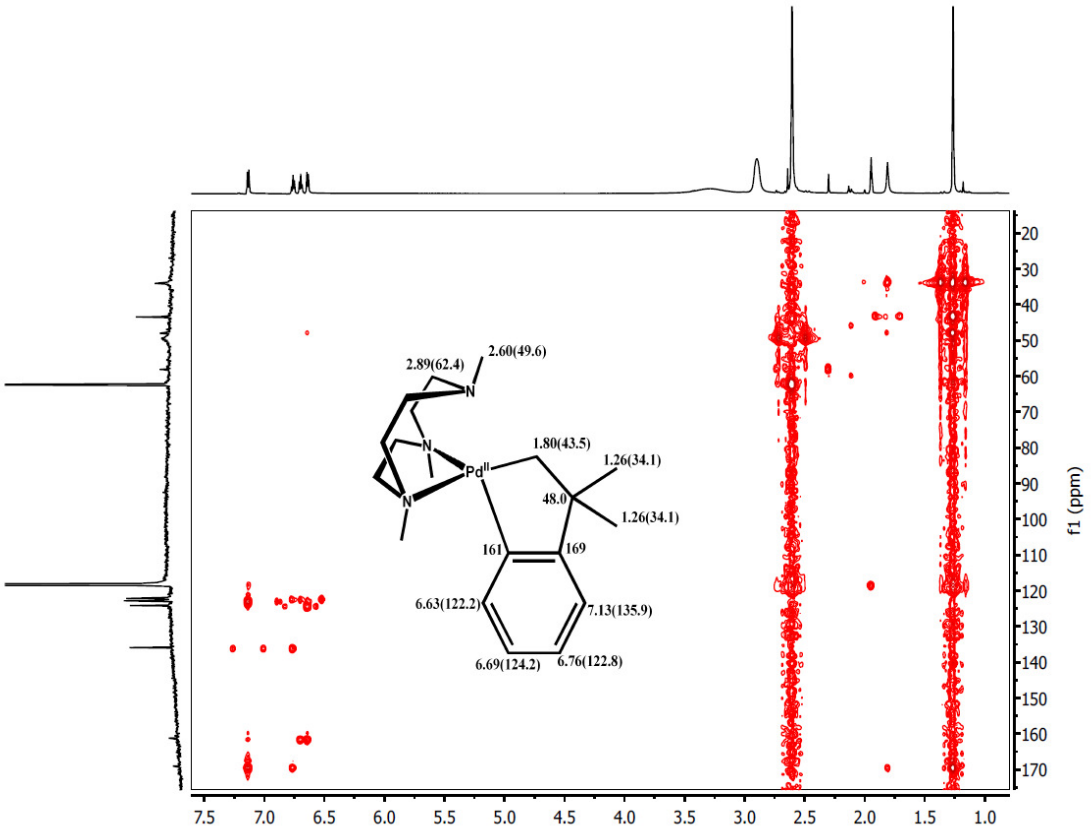


Figure S2. ^{1}H-^{13}C HMBC spectrum of compound **1** in CD_3CN.

[(Me$_3$tacn)Pd^{IV}(OH)(CH$_2$CMe$_2$C$_6$H$_4$)]ClO$_4$ ([2]ClO$_4$). To a stirred solution of **1** (28.8 mg, 0.070 mmol) in MeCN (2 mL), aqueous H_2O_2 (50 wt%, 0.020 mL, 0.35 mmol) was added. The resulting solution was stirred for 10 min. Then $LiClO_4$ (22 mg, 0.21 mmol) was added to the clear brown red solution. The cloudy solution was filtered after 30 min. Diethyl ether was diffused into the filtrate over a few days. Brown crystals formed were collected, washed with ether, pentane, and dried under high vacuum. Yield: 20.3 mg, 0.0389 mmol, 56%.

Alternate synthesis: O_2 was bubbled into a stirred solution of **1** (30.0 mg, 0.073 mmol) in MeCN (2 mL), followed by addition of 5 equiv of 35% HCl. To the resulting brown solution 3 equiv of $LiClO_4$ (22 mg, 0.21 mmol) was added to the solution. Diethyl ether was allowed to diffuse into the reaction solution overnight and the resulting crystals were collected, washed with ether, pentane, and dried under high vacuum. Yield: 30.0 mg, 78.5%.

^{1}H NMR (600 MHz, CD_3CN), δ: 7.50 (d, *J* = 8.0 Hz, 1H, Ph-H), 7.16 (t, *J* = 7.4 Hz, 1H, Ph-H), 7.10 (t, *J* = 7.8 Hz, 1H, Ph-H), 6.98 (d, *J* = 7.5 Hz, 1H, Ph-H), 4.05 (d, *J* = 6.2 Hz, 1H, $PdCH_2$), 3.97 (d, *J* = 6.2 Hz, 1H, $PdCH_2$), 3.28-2.82 (m, 8H, $-CH_2-$) 2.92 (s, 3H, N-CH_3), 2.76 (s, 3H, N-CH_3), 2.27 (s, 3H, N-CH_3), 1.39 (s, 6H, CMe_2). ^{13}C NMR (151 MHz, CD_3CN), δ: 163.8, 153.9, 130.8, 128.1, 127.9, 127.2, 74.9, 65.0, 61.1, 59.6, 58.4, 56.8, 53.8, 53.2, 49.0, 48.6, 35.1, 32.1. ESI-MS (m/z): 426.1724, Calcd for $[(Me_3tacn)Pd^{IV}(OH)(CH_2CMe_2C_6H_4)]^+$ 426.1737. Anal. Found: C, 43.88; H, 6.46; N, 8.07. Calcd for $C_{19}H_{34}ClN_3O_5Pd$: C, 43.35; H, 6.51; N, 7.98.

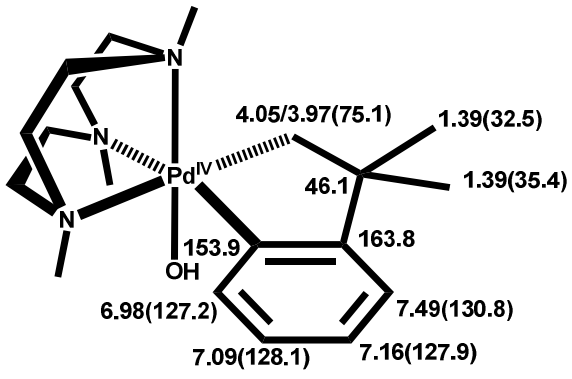
Aerobic oxidation of 1.

Method A. Oxidation in MeCN-H_2O solution.

To the solution of **1** (2 mg, 0.0049 mmol) in CD_3CN (0.5 mL) in a NMR tube, O_2 was bubbled for 30 seconds. Then 55 μL of D_2O was added and the NMR tube was filled with O_2 and capped. The solution was mixed thoroughly, and the reaction was monitored periodically by NMR up to 17 hrs. NMR indicated the yield of product **2** reached 48%. The counter anion for complex **2** is most likely hydroxide formed by O_2 reduction in presence of water.

Method B. Oxidation in presence of a buffer solution.

To the solution of **1** (2 mg, 0.0049 mmol) in CD_3CN (0.5 mL) in a NMR tube, O_2 was bubbled for 30 seconds. Then 55 μL of the 1 M phosphate buffer in D_2O (pD = 7.43) was added. The NMR tube was filled with O_2 and capped. The solution was mixed thoroughly, and NMR was taken in 5 minutes. NMR indicated that all starting material was converted to product **2**. Yield: 98%.



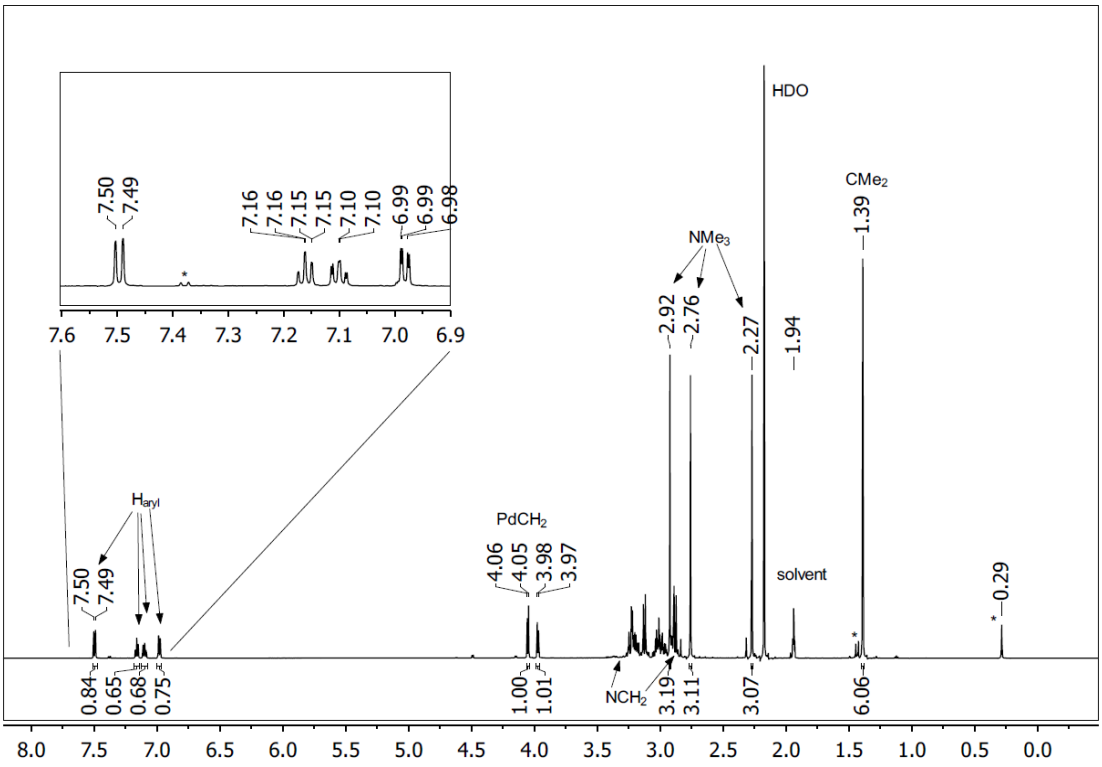


Figure S3. ^{1}H NMR of compound **[2]ClO$_4$** in CD_3CN. Peaks labeled with asterisks are unidentified impurities.

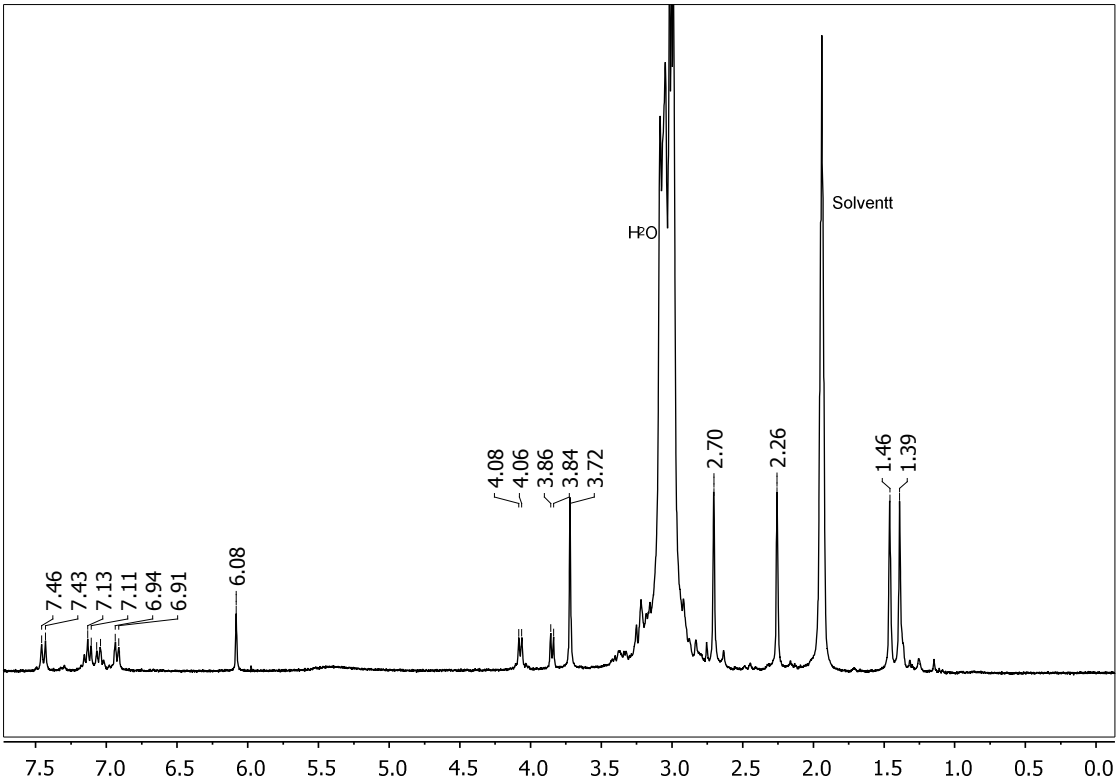


Figure S4. Aerobic oxidation of $(Me_3tacn)Pd^{II}(CH_2CMe_2C_6H_4)$, **1**, in presence of 10% 1.0 M phosphate buffer in D_2O (pD = 7.43). The spectrum was obtained after 5 min, and the starting material was completely converted to product **2**.

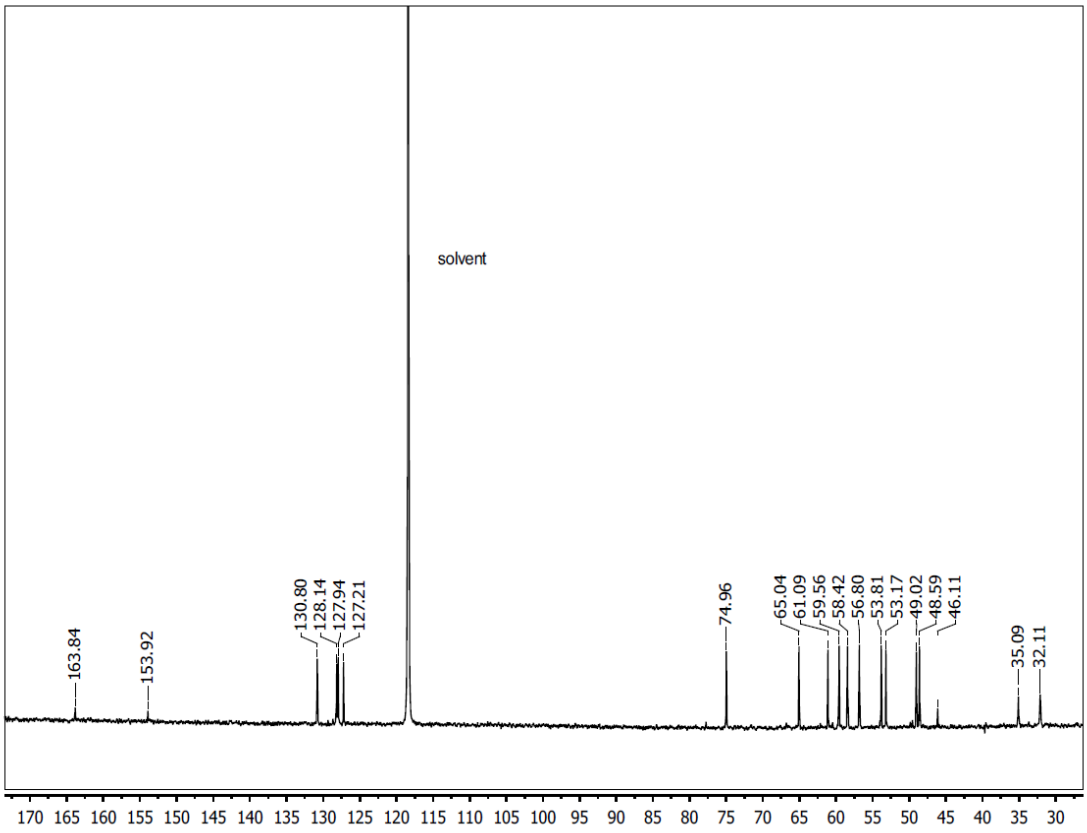


Figure S5. ^{13}C NMR of compound [**2**]$\mathbf{ClO_4}$ in CD_3CN.

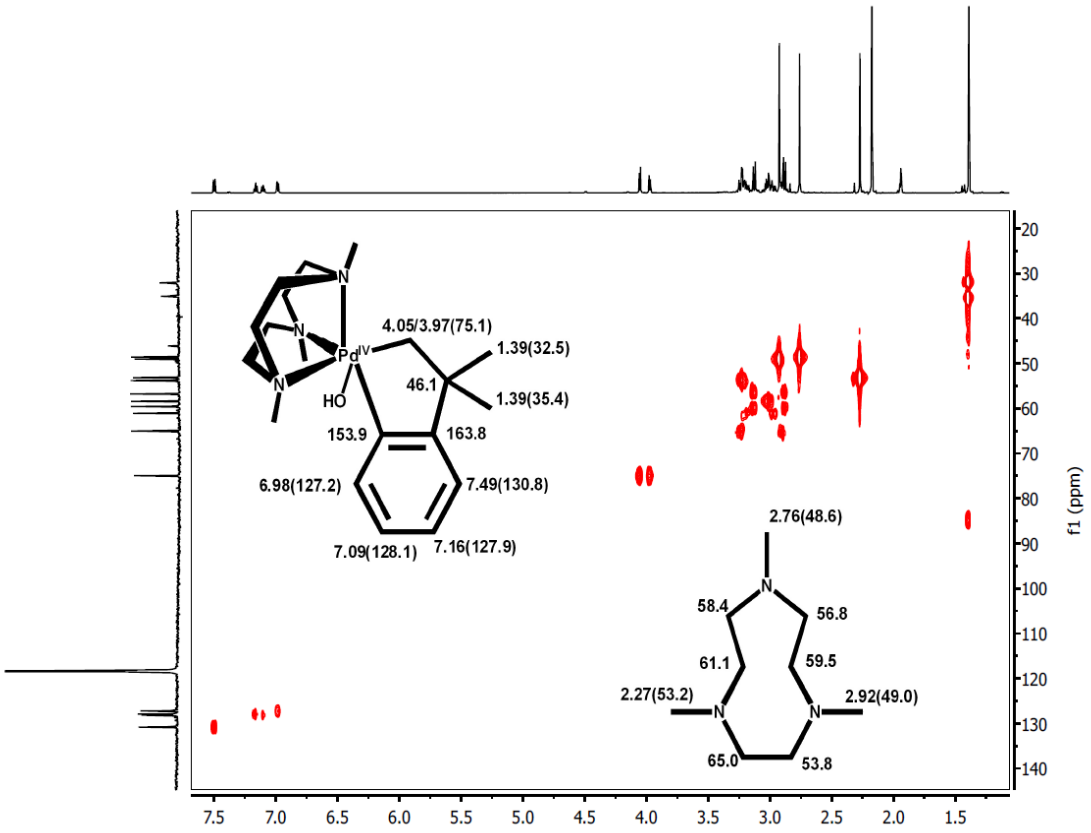


Figure S6. ^{1}H-^{13}C HSQC spectrum of compound **[2]ClO$_4$** in CD_3CN.

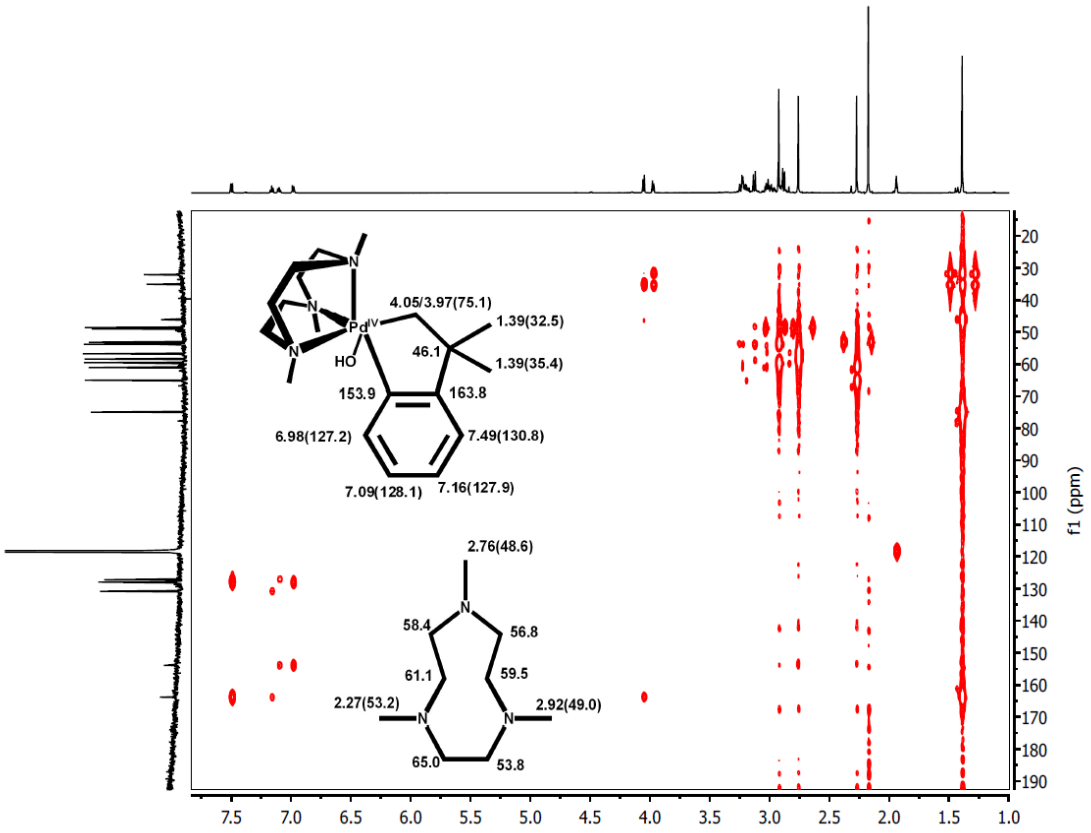


Figure S7. ^{1}H-^{13}C HMBC spectrum of compound **[2]ClO$_4$** in CD_3CN.

Preparation of [(Me$_3$tacn)Pd^{IV}(F)(CH$_2$CMe$_2$C$_6$H$_4$)]OTf ([5]OTf).

To a stirred solution of **1** (35 mg, 0.085 mmol) in MeCN (5 mL), 1-fluoro-2,4,6-trimethylpyridinium triflate (25 mg, 0.085 mmol, 1 eq) was added. The light yellow solution turned intense dim brown quickly. After stirring for 5 min, the solution was filtered, evaporated under vacuum to give yellow oil. The yellow oil was dissolved in DCM, and diethyl ether was added to precipitate the product. The top clear solvent was decanted and the remaining sticky solid residue was redissolved in DCM and dried under high vacuum to give foamy product, which was washed with pentane to remove the residual DCM, and dried under high vacuum again. Yield: 28.3 mg, 0.049 mmol, 58%.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.38 (d, J = 8.1 Hz, 1H, Ph-H), 7.17 (t, J = 6.8 Hz, 1H, Ph-H), 7.10 (dd, J = 11.5, 3.7 Hz, 1H, Ph-H), 6.96 (dd, J = 7.4, 2.0 Hz, 1H, Ph-H), 4.36 (dd, J = 10.4, 5.3 Hz, 1H, Pd-CH_2), 4.17 (m, 1H, Pd-CH_2), 3.88-2.51 (m, 12 H, NCH_2)3.11 (s, J = 5.2 Hz, 3H,

NCH_3), 2.94 (s, *J* = 4.7 Hz, 3H, NCH_3), 2.38 (s, 3H, NCH_3), 1.48 (s, 3H, C*Me*), 1.44 (s, 3H, C*Me*). ^{19}F NMR (282 MHz, $CDCl_3$), δ: -78.36 (s, OTf), -337.01 (s, Pd-F). ESI-MS (m/z): 428.1701; Calcd for $[(Me_3tacn)Pd^{IV}(F)(CH_2CMe_2C_6H_4)]^+$: 428.1695. Anal. Found: C, 41.28; H, 6.67; N, 7.59. Calcd for $C_{20}H_{33}FN_3O_3PdS$: C, 41.56; H, 5.75; N, 7.27. The higher than expected hydrogen value is probably due to the presence of HF, a side product resulting from $(Me_3tacn)Pd(CH_2CMe_2C_6H_4)$ reacting with F^+.

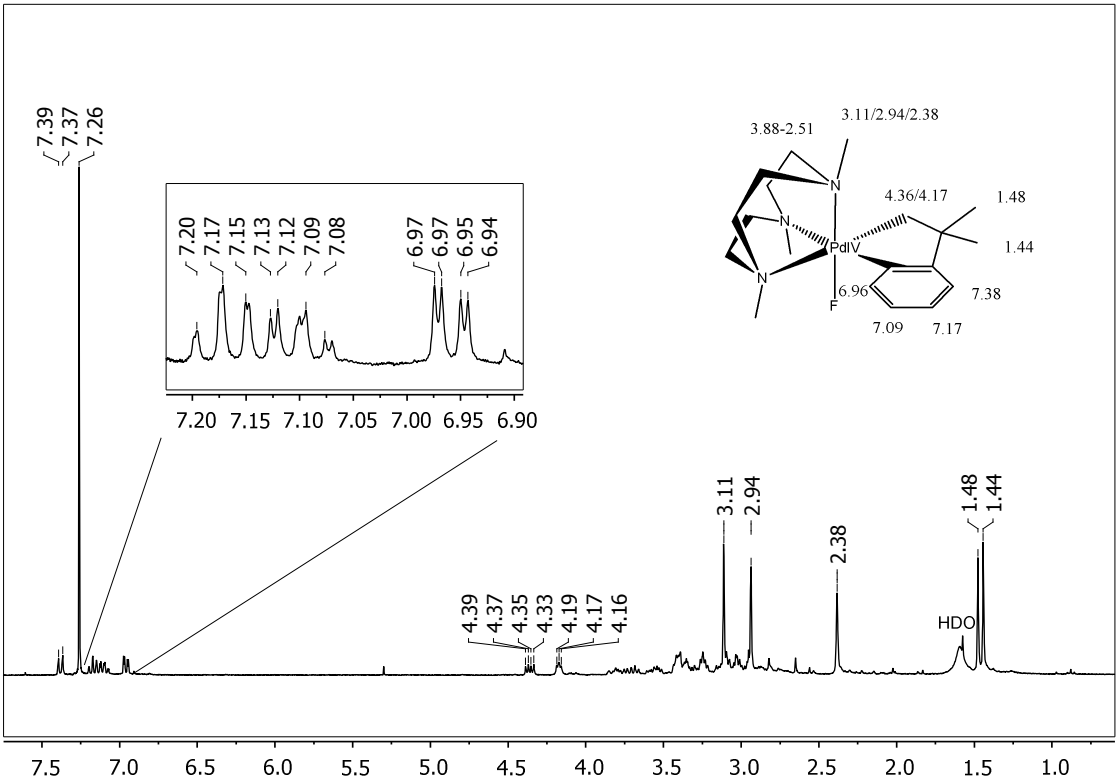


Figure S8. ^1H NMR of compound **[5]OTf** in $CDCl_3$.

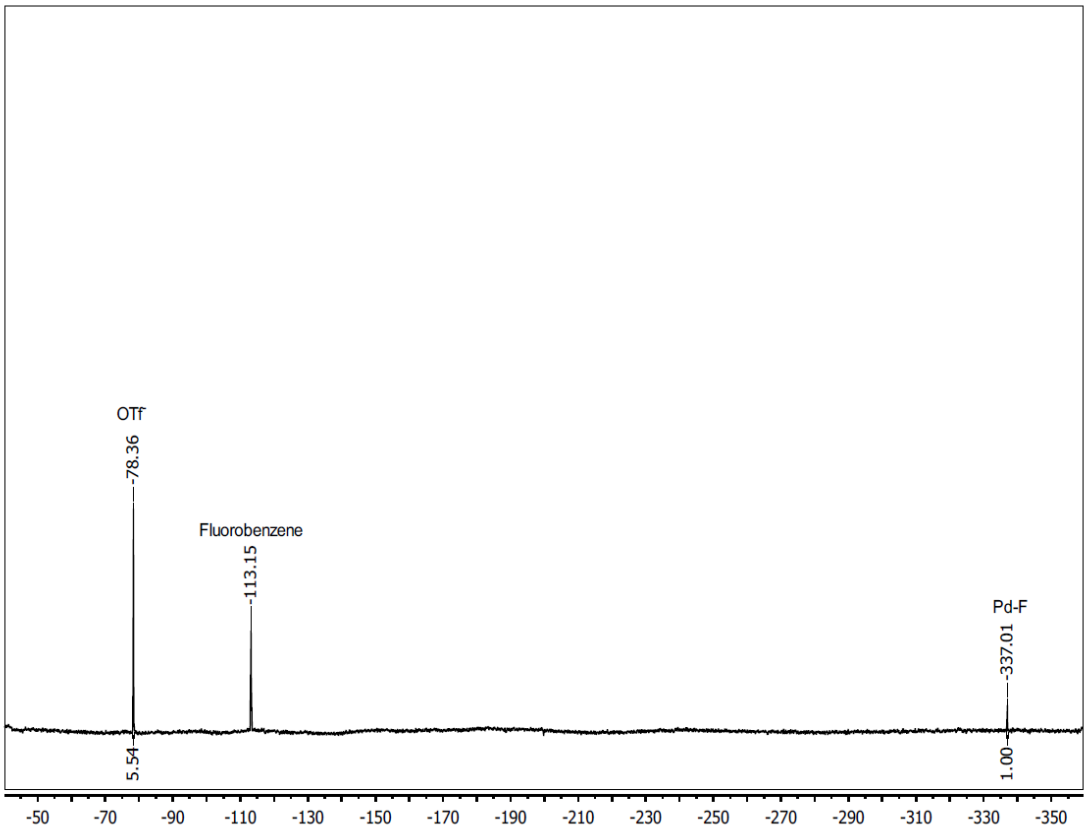


Figure S9. ^{19}F NMR of compound **[5]OTf** in $CDCl_3$. Fluorobenzene was added as an internal reference to the solution.

Preparation of $[(Me_3tacn)Pd^{IV}(Cl)(CH_2CMe_2C_6H_4)]ClO_4$ ([6]ClO_4).

To a stirred solution of **1** (30.0 mg, 0.0724 mmol) in MeCN (1 mL), $PhICl_2$ (20.0 mg, 0.0724 mmol, 1 eq) was added. After stirring for 5 minutes, the solution was filtered. To the resulting clear yellow solution, $LiClO_4$ (23.1 mg, 0.217 mmol, 3 eq) was added. The solution was stirred for another 5 minutes and filtered again. To the filtrate, large amount of ether was added to precipitate the product. After settled down, the top solution was decanted and the bottom powder was washed with ether, then pentane. The resulted yellow powder was dried under vacuum. Yield: 12 mg, 0.025 mmol, 34%. ^1H NMR (300 MHz, CD_3CN), δ: 7.38 (dd, J = 8.0, 1.2 Hz, 1H, Ph-H), 7.16 (td, J = 7.3, 1.2 Hz, 1H, Ph-H), 7.09 (td, J =7.8, 2.1 Hz, 1H, Ph-H), 6.99 (dd, J = 7.3, 2.1 Hz, 1H, Ph-H), 4.49 (d, J = 5.7 Hz, 1H, Pd-CH_2), 4.15 (d, J = 5.7 Hz, 1H, Pd-CH_2), 3.43-

2.85 (m, 12H, NCH_2), 3.03 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3), 2.32 (s, 3H, NCH_3), 1.45 (s, 3H, C*Me*), 1.43 (s, 3H, C*Me*).

ESI-MS (m/z): 446.1; Calcd for $[(Me_3tacn)Pd^{IV}(Cl)(CH_2CMe_2C_6H_4)]^+$: 446.1. Anal. Found: C, 42.12; H, 6.08; N, 7.69. Calcd for $C_{19}H_{33}Cl_2N_3O_4Pd$: C, 41.89; H, 6.11; N, 7.71.

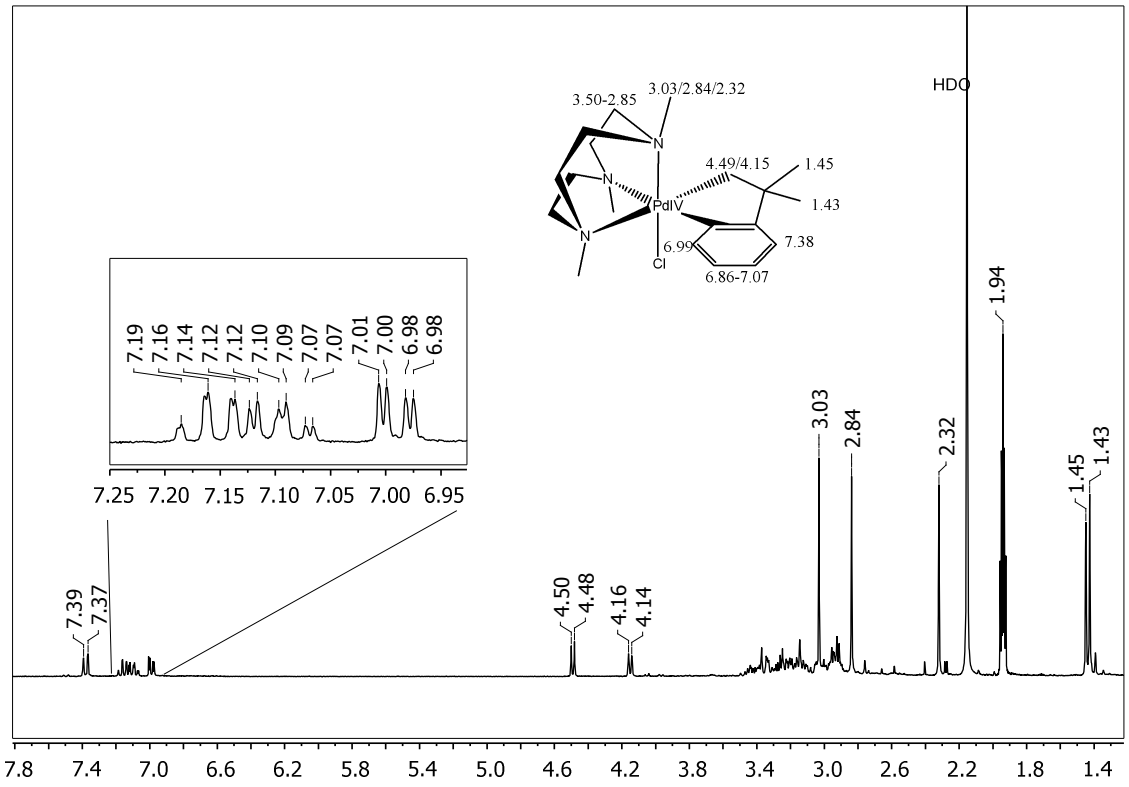


Figure S10. ^1H NMR of compound **[6]ClO$_4$** in CD_3CN.

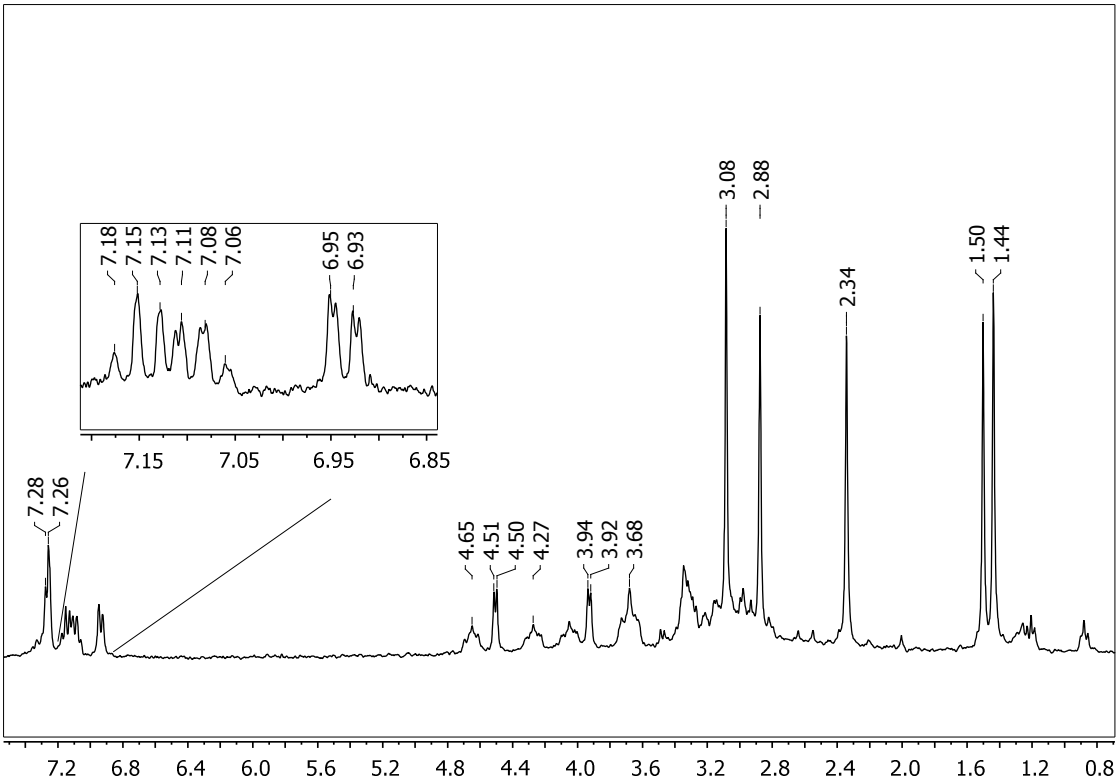


Figure S11. ^{1}H NMR of compound **[6]ClO$_4$** in $CDCl_3$.

Preparation of [(Me$_3$tacn)Pd^{IV}(I)(CH$_2$CMe$_2$C$_6$H$_4$)]I ([7]I).

To a stirred solution of **1** (15.8 mg, 0.0385 mmol) in acetone (1 mL), I_2 (10.0 mg, 0.0385 mmol, 1 eq) was added. Orange precipitate formed quickly. After stirring for 1 h, the orange powder was collected by suction filtration, dried under high vacuum. Yield: 14.6 mg, 0.022 mmol, 57%. ^{1}H NMR (300 MHz, CD_3CN), δ: 7.28 (dd, *J* = 7.7, 1.5 Hz, 1H, Ph-H), 7.14 – 7.02 (m, 2H, Ph-H), 6.97 (dd, *J* = 6.9, 2.5 Hz, 1H, Ph-H), 4.77 (d, *J* = 6.2 Hz, 1H, Pd-CH_2), 3.88 (d, *J* = 6.2 Hz, 1H, Pd-CH_2), 3.55 - 2.73 (m, 12 H, NCH_2), 3.20 (s, 3H, NCH_3), 3.04 (s, 3H, NCH_3), 2.08 (s, 3H, NCH_3), 1.43 (s, 3H, C*Me*), 1.40 (s, 3H, C*Me*).

ESI-MS (m/z): 536.0750; Calcd for [(Me$_3$tacn)Pd^{IV}(I)(CH$_2$CMe$_2$C$_6$H$_4$)]$^+$: 536.0754. Anal. Found: C, 34.45; H, 5.67; N, 6.20. Calcd for $C_{19}H_{33}I_2N_3Pd$: C, 34.38; H, 5.01; N, 6.33.

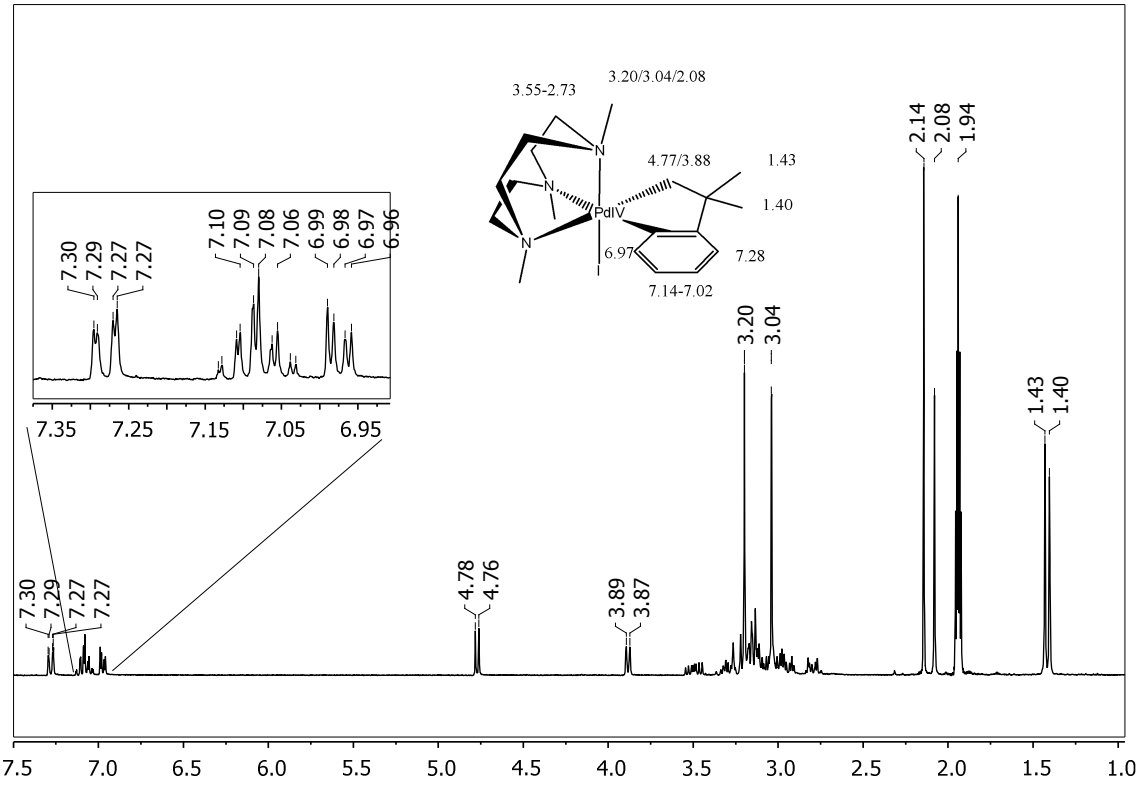


Figure S12. ^{1}H NMR of compound [**7**]**I** in CD_3CN.

III. Cyclic voltammograms of 1.

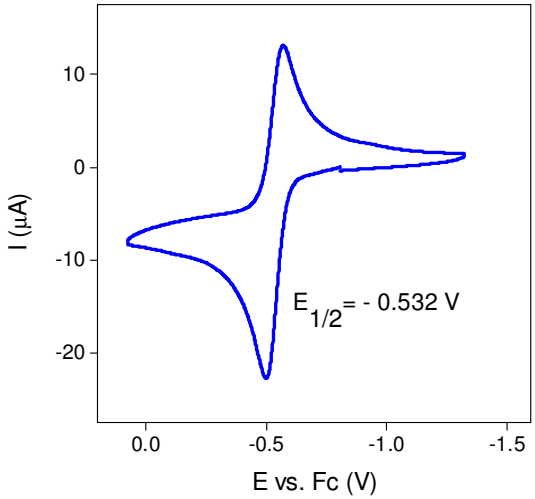


Figure S13. Cyclic voltammogram of $(Me_3tacn)Pd^{II}(CH_2CMe_2C_6H_4)$, **1**, in 0.1 M Bu_4NPF_6/MeCN (v = 100 mV/s). $E_{1/2}$ = -0.532 V (ΔE_p = 71 mV) vs. Fc^+/Fc. Coulometry measurements reveal that the anodic wave corresponds to a $2e^-$ oxidation.

Interestingly, the presence of a coordination anion affects the electrochemical behavior of **1**. For example, when 1 equivalent of Br^- is added, the oxidation and reduction peaks shift more negatively by 0.15 V and 0.31 V, respectively (Figure S14). The lower potential observed in presence of Br^- can be attributed to the product stabilization via coordination of an exogenous Br^- anion to produce a monocationic Pd^{IV} center, while in the absence of a strongly coordinating ion the product is likely a less stable, dicationic Pd^{IV} species with a coordinated solvent in the axial position. Similar behavior was observed in presence of Cl^- or OH^- as external anions.

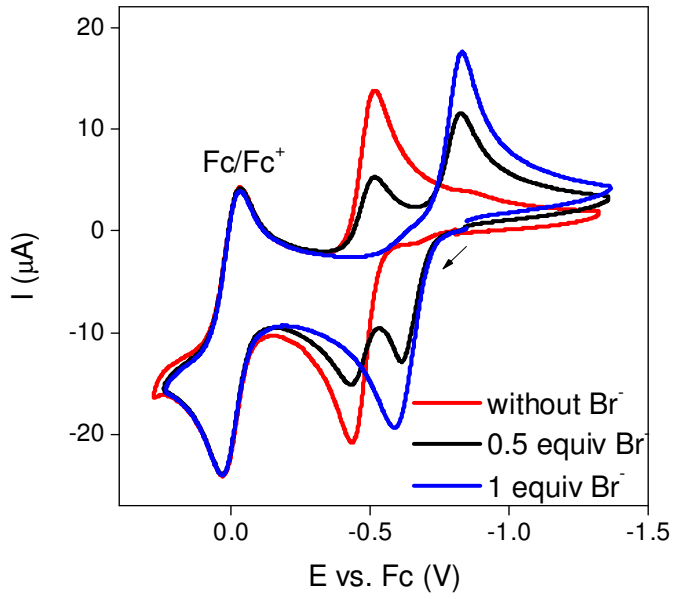


Figure S14. Cyclic voltammogram of $(Me_3tacn)Pd^{II}(CH_2CMe_2C_6H_4)$, **1**, in presence of various amount of Br^-, in 0.1 M Bu_4NPF_6/MeCN (v = 100 mV/s).

IV. ESI-MS studies of aerobic oxidation of 1

The ESI-MS experiments were performed using either a Bruker Maxis Q-TOF or a Thermo LTQ-FT mass spectrometer, both with an electrospray ionization source. 0.1 mg of $(Me_3tacn)Pd(CH_2CMe_2C_6H_4)$ were dissolved in 0.5 mL of 5% H_2O/MeCN at RT. The reaction solutions were then periodically analyzed by ESI-MS by direct injection of 50 μL of the solution into the ESI-MS instrument. Two peaks with m/z values of at 426.1732 and 442.1685 were observed at the early stages of the reaction. The two peaks were of 1:10 ratio at 1h. And the second peak decreased over time, accompanied by the increase of the first peak. The ratio became around 1:3 at 1 day. The two peaks were assigned to $[(Me_3tacn)Pd^{IV}(CH_2CMe_2C_6H_4)(OH)]^+$ (**2**, calcd $C_{19}H_{34}N_3O^{106}Pd^+$ 426.1739) and $[(Me_3tacn)Pd^{IV}(CH_2CMe_2C_6H_4)(OOH)]^+$ (**3**, calcd $C_{19}H_{34}N_3O_2{}^{106}Pd^+$ 442.1688), respectively.

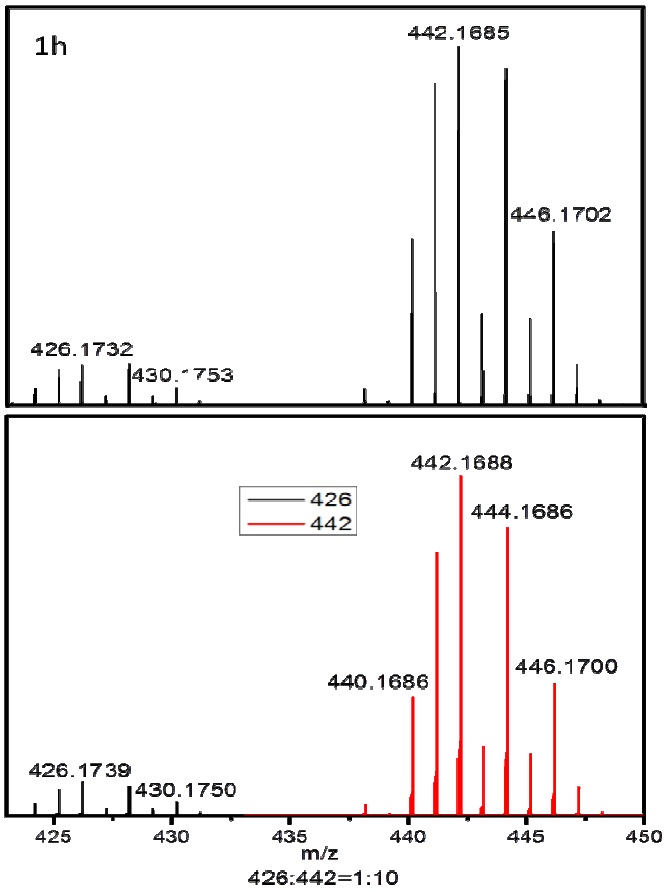


Figure S15. ESI-MS spectra for the aerobic oxidation of $(Me_3tacn)Pd^{II}(CH_2CMe_2C_6H_4)$, **1**, in 5% H_2O/CH_3CN, after 1 h (top) and simulation using a **2**:**3** ratio of 1:10.

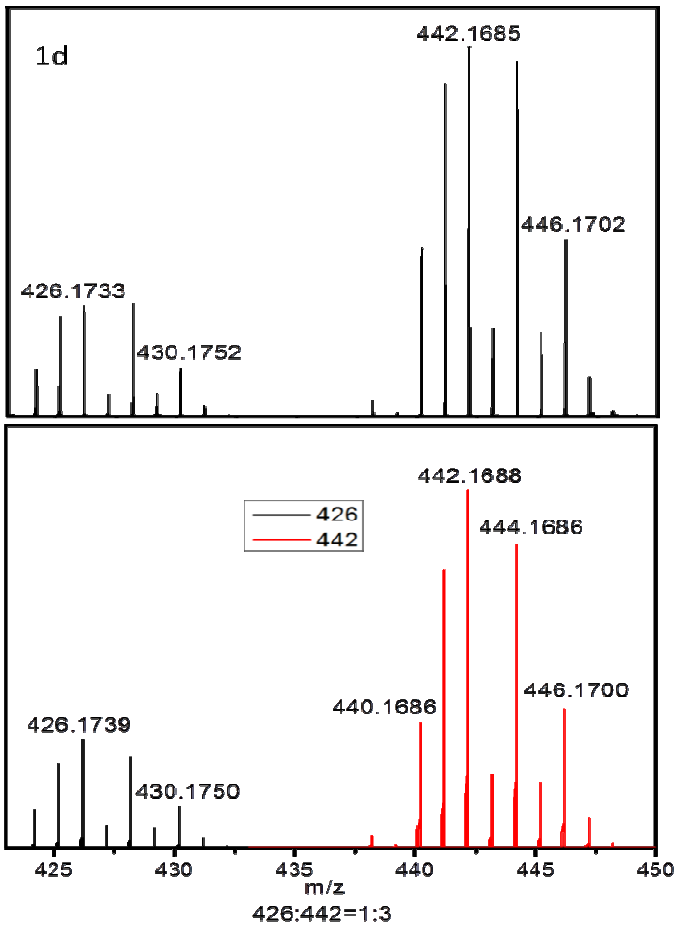


Figure S16. ESI-MS spectra for the aerobic oxidation of $(Me_3tacn)Pd^{II}(CH_2CMe_2C_6H_4)$, **1**, in 5% H_2O/CH_3CN, after 1 day (top) and simulation using a **2**:**3** ratio of 1:3.

V. Reactivity of $(Me_3tacn)Pd^{IV}$ complexes

Thermolysis of $[Me_3tacnPd^{IV}(OH)(CH_2CMe_2C_6H_4)]ClO_4$ ($[2]ClO_4$).

A stock solution of **[2]ClO_4** was prepared in DMSO-d_6. The stock solution was transferred into a NMR tube, followed by addition of the 1,3,5-trimethoxybenzene as the internal standard. The NMR tube was sealed and heatet, and the solution was periodically analyzed by NMR. The heating continued until no further changes were observed. The yields of the products were determined by NMR integration vs. internal standard, calculated as [moles of product]/[moles of **2**]*100%. The Pd product was not identified as it is not soluble in DMSO, and precipitate was observed at the end of the reaction. In addition, no NMR signals corresponding to Me_3tacn were observed after the thermolysis was complete.

Formation of compound 2-tert-butylphenol was confirmed by addition of an authentic sample at the end of the reaction. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 9.27 (s, 1H), 7.12 (d, *J* = 7.8, 1H), 6.98 (t, *J* = 7.5, 1H), 6.76 (d, *J* = 8.0, 1H), 6.69 (t, *J* = 7.4, 1H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 155.8, 135.2, 126.7, 126.2, 118.6, 116.1, 34.2, 29.3.

GC-MS analysis procedure:

The reaction solution was cooled down to RT. Then it was treated with 3 mL of $HClO_4$, followed by extraction with ether (3 x 1 mL). The ether layer were combined and washed with saturated aqueous $NaHCO_3$ solution, followed by washing with brine. The final ether solution was dried over K_2CO_3. Then 1 μL of the final solution was injected into GC-MS for analysis.

Reaction in the presence of D_2O.

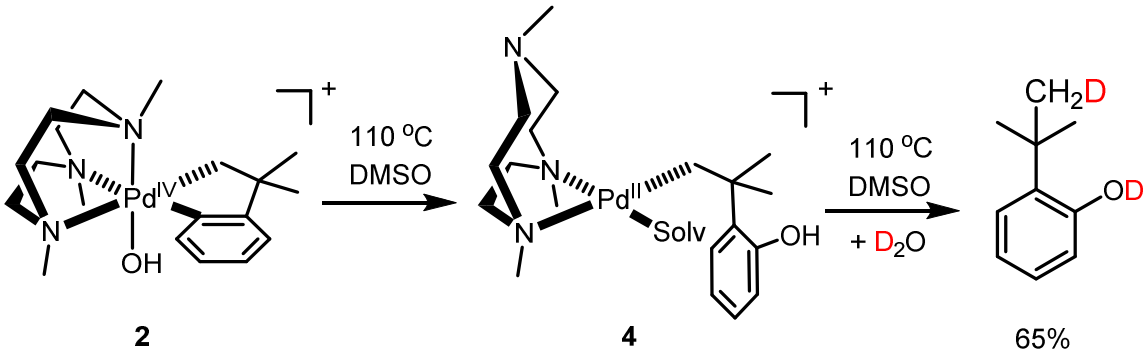
The analogous procedure was used for the reaction in the presence of 55 μL of D_2O in 0.5 mL of DMSO-d_6. The product 2-tert-butylphenol, was isolated as following. The reaction solution was treated with 3 mL of $HClO_4$, then the solution was extracted by ether (3 x 1 mL). The ether layer were combined and washed with saturated aqueous $NaHCO_3$ solution, followed by washing with brine. The final ether solution was dried over K_2CO_3. Then 1 μL of the final solution was injected into GC-MS for analysis. The OD group exchanged with OH group during this procedure. The GC-MS analysis shows that deuterium was incorporated into one of the methyl groups of the tert-butyl group in 2-tert-butylphenol:

GC-MS, m/z (relative abundance): 151 (66, M), 136 (100, M - CH_3), 135 (65, M - CH_2D), 108 (68, M - 3 CH_3), 107 (98, M - $(CH_3)_2CH_2D$) (Figure S24, top).

For comparison, GC-MS of the non-deuterated 2-tert-butylphenol product has the following fragmentation pattern (Figure S24, bottom):

GC-MS, m/z (relative abundance): 150 (33, M), 135 (96, M - CH_3), 107 (100, M - 3 CH_3).

In addition, tBu group appears in a NMR spectrum as two unresolved multiplets assigned as two CH_3 groups and a slightly downfield shifted CH_2D group, with relative integration ratio of ~5.6 : 2 (Figure S23). This experiment shows that trace water present in DMSO-d_6 (~ 35 mM of H_2O in DMSO-d_6) likely acts as a source of protons for the formation of 2-tert-butylphenol. However, when D_2O (10%) was deliberately added to DMSO-d_6, thermolysis of **[2]ClO$_4$** gave 2-tert-butylphenol in 65% yield, which indicated more water did not lead to higher yield.



Scheme S1. Thermolysis of **[2]ClO$_4$** in presence of 10% D_2O.

Thermolysis of [2]ClO_4 at different initial concentration.

Complex **[2]ClO_4** (1.1 mg, 0.00209 mmol) was dissolved in 0.4 mL of DMSO-d_6 and 1,3,5-trimethoxybenzene was added as the internal standard. The solution was transferred into a NMR tube, capped, and sealed to give the final concentration of 5.22 mM. Similarly, solutions of concentration of 9.499 mM and 19.47 mM were prepared by dissolving 2.0 mg and 4.1 mg of **[2]ClO_4** in 0.4 mL of DMSO-d_6, respectively. The NMR tube was heated and periodically analyzed by NMR. The heating continued until no further changes were observed. The yields of the products were determined by NMR integration vs. internal standard, calculated as [moles of product]/[moles of **2**]*100%. A small amount (<10%) of unidentified side products was observed by NMR.

Note: The highest yield (74%) was obtained at a concentration of **2** or 5.22 mM, while the lowest yield (57%) was obtained at 19.5 mM **2**. This suggests that C_{alkyl}-O bond formation most likely does not follow a bimolecular mechanism, however bimolecular side-reactions may lead to a decreased yield of 2-tert-butylphenol at higher concentrations of **2**.

Starting conc. of **[2]ClO_4**	5.22 mM	9.499 mM	19.47 mM
Yield of 2-tert-butylphenol	74.1%	66.2%	55.6%

Thermolysis of [2]ClO_4 in DMSO at 110 ^oC.

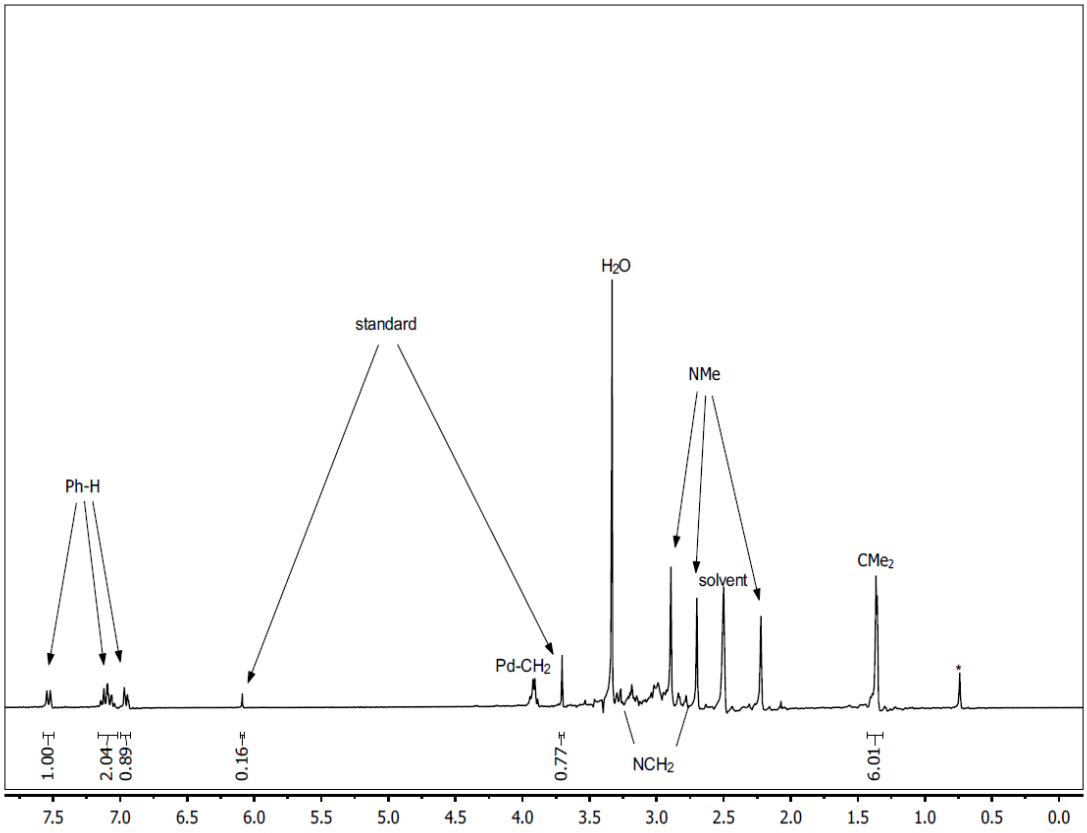


Figure S17. ^1H NMR of thermolysis of compound **[2]ClO_4** in DMSO-d_6: Before heating. 1,3,5-trimethoxybenzene was used as internal standard. Peak(s) labeled with asterisk are unidentified impurities from starting material.

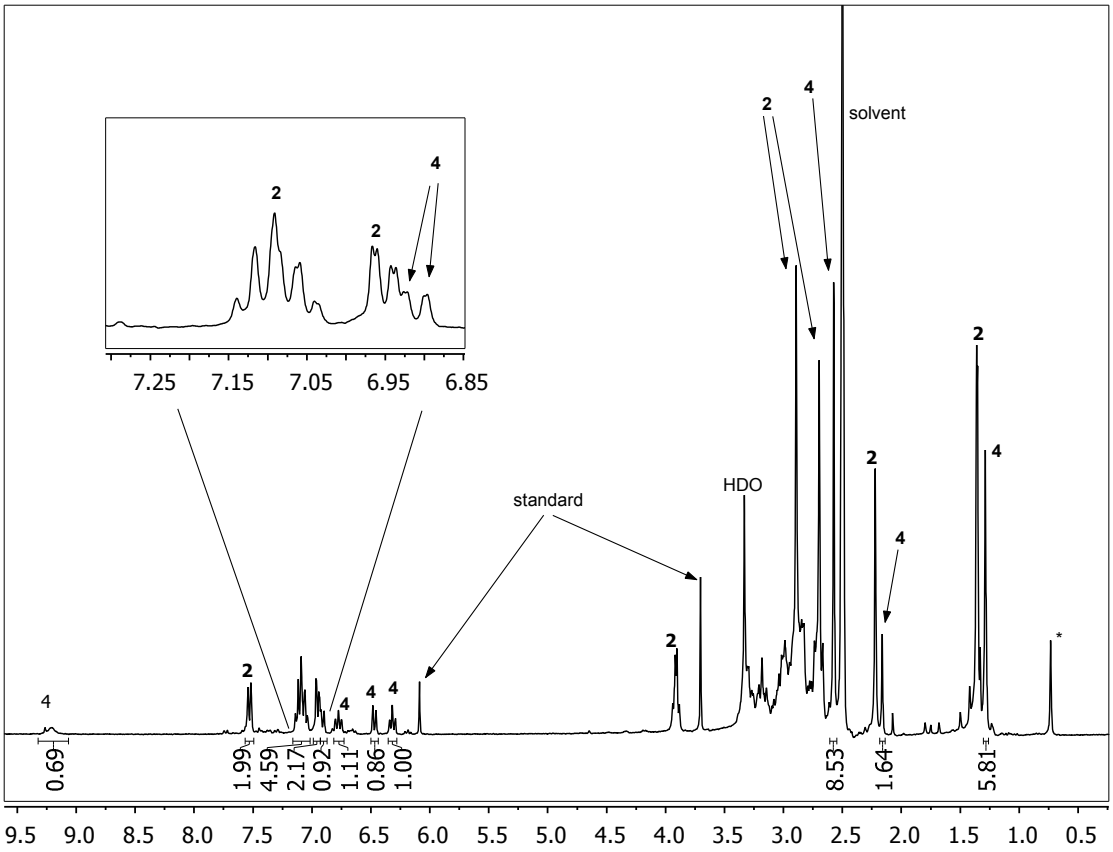


Figure S18. ^{1}H NMR of thermolysis of compound **[2]ClO$_4$** in DMSO-d$_6$: After heating at 110 ^{o}C for 30 minutes. 1,3,5-trimethoxybenzene was used as internal standard. Peak(s) labeled with asterisk are unidentified impurities from starting material.

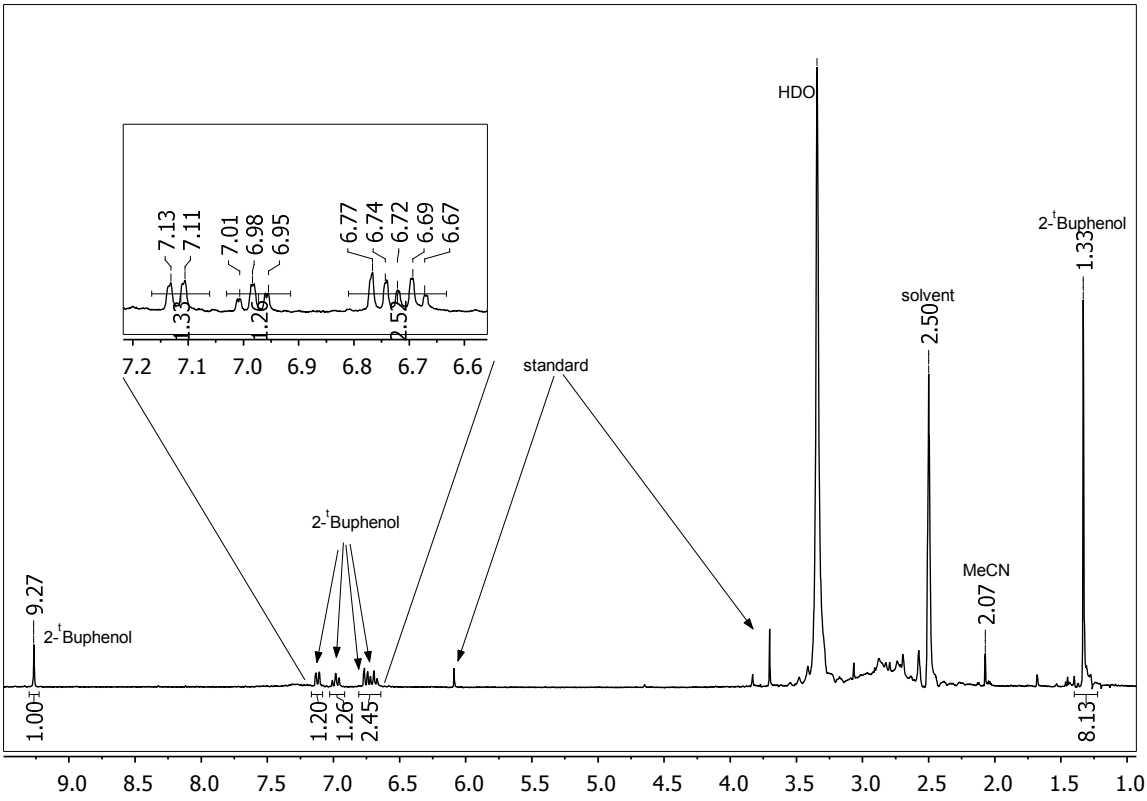


Figure S19. ^{1}H NMR of thermolysis of compound **[2]ClO$_4$** in DMSO-d$_6$: heated at 110 ^{o}C for 4 hrs to give 2-tert-butylphenol.

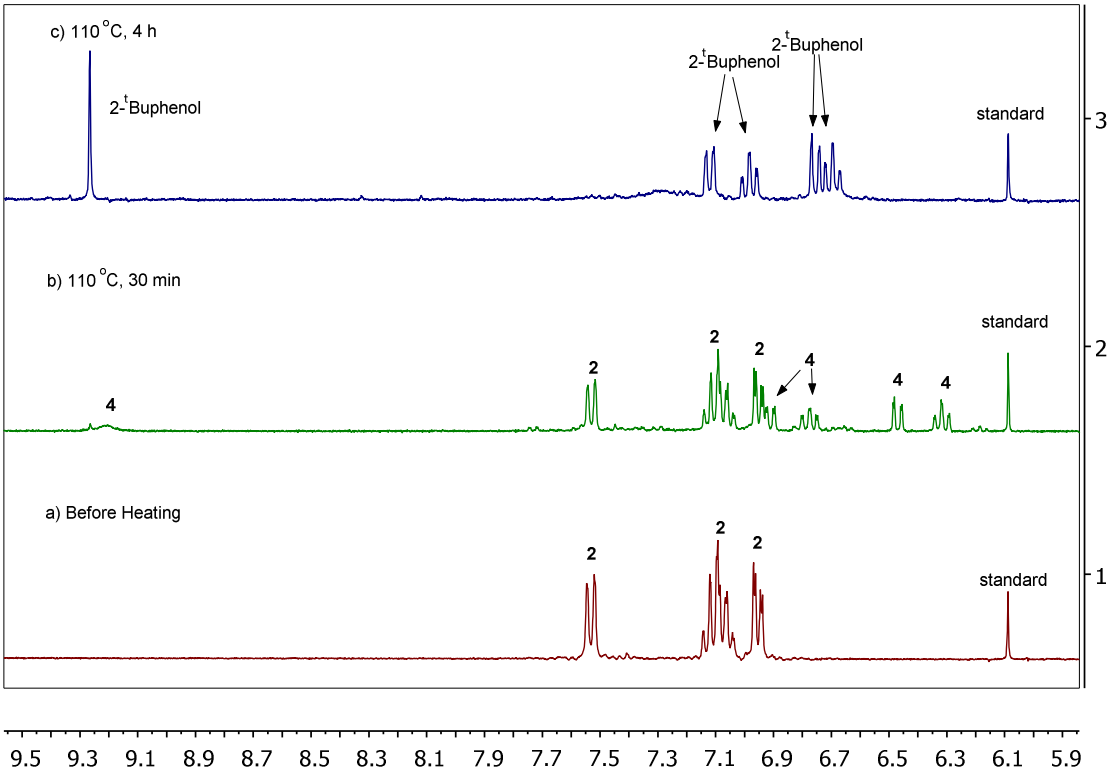


Figure S20. ^{1}H NMR of thermolysis of compound **[2]ClO$_4$** in DMSO-d$_6$. a) before heating. b) heated at 110 °C for 30 minutes. c) heated at 110 °C for 4 h.

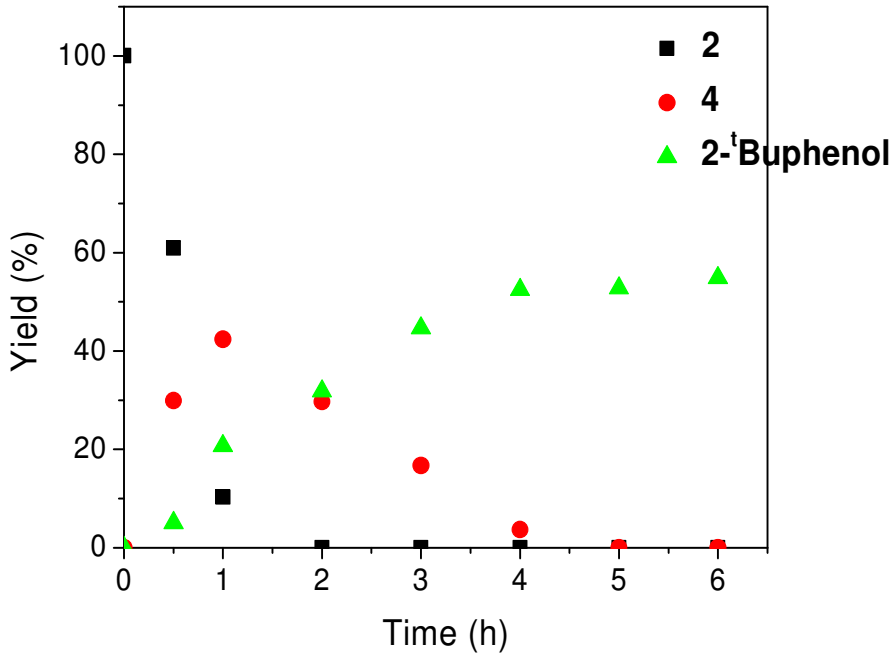


Figure S21. Yields of **4** and 2-tert-butylphenol during the thermolysis of **[2]ClO$_4$** determined by NMR.

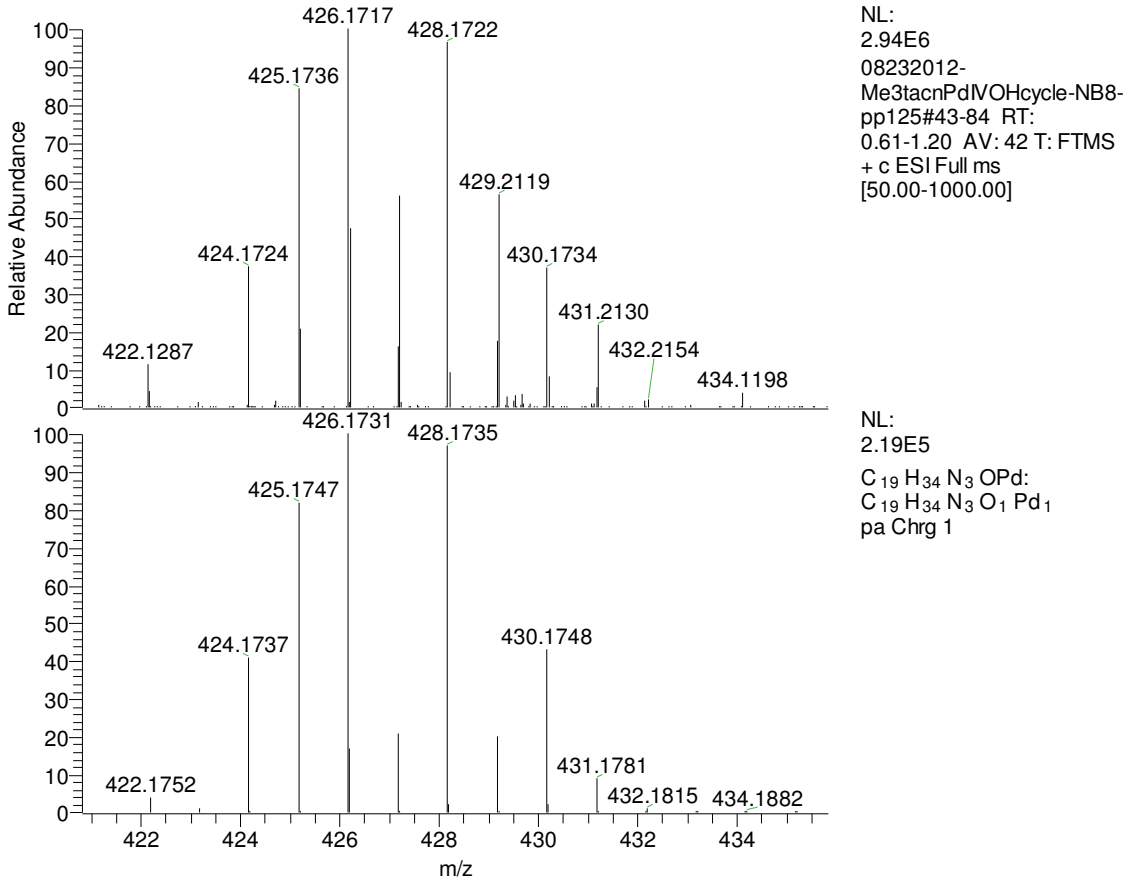


Figure S22. ESI-MS spectra of thermolysis of **[2]ClO$_4$** at 110 ^{o}C after 2 hrs. Starting material **[2]ClO$_4$** has reacted completely, as observed by NMR. Top: observed isotopic pattern; bottom: calculated isotopic patter from [(Me$_3$tacn)Pd^{II}(CH$_2$CMe$_2$-*o*-OH-C$_6$H$_4$)]$^+$ (**4**). Note: The reaction mixture was diluted with MeCN and analyzed by ESI-MS.

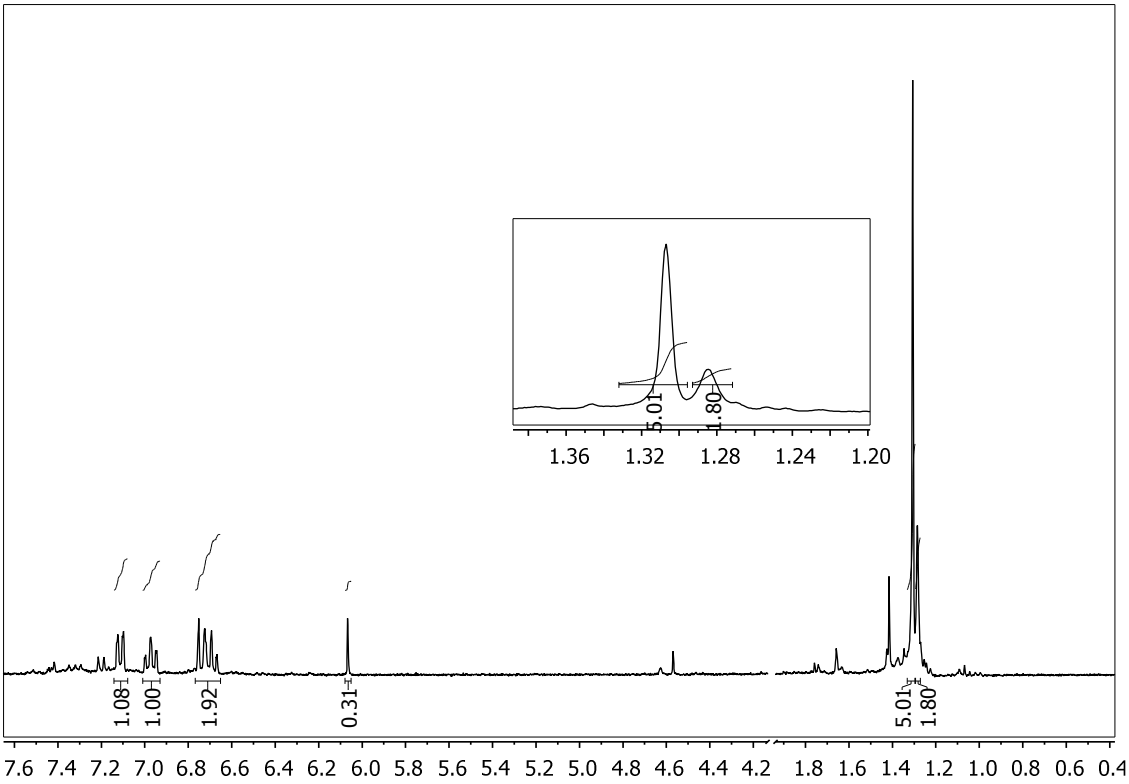


Figure S23. ^{1}H NMR of thermolysis of compound [**2**]**ClO$_4$** in DMSO-d$_6$ in presence of 10% of D_2O.

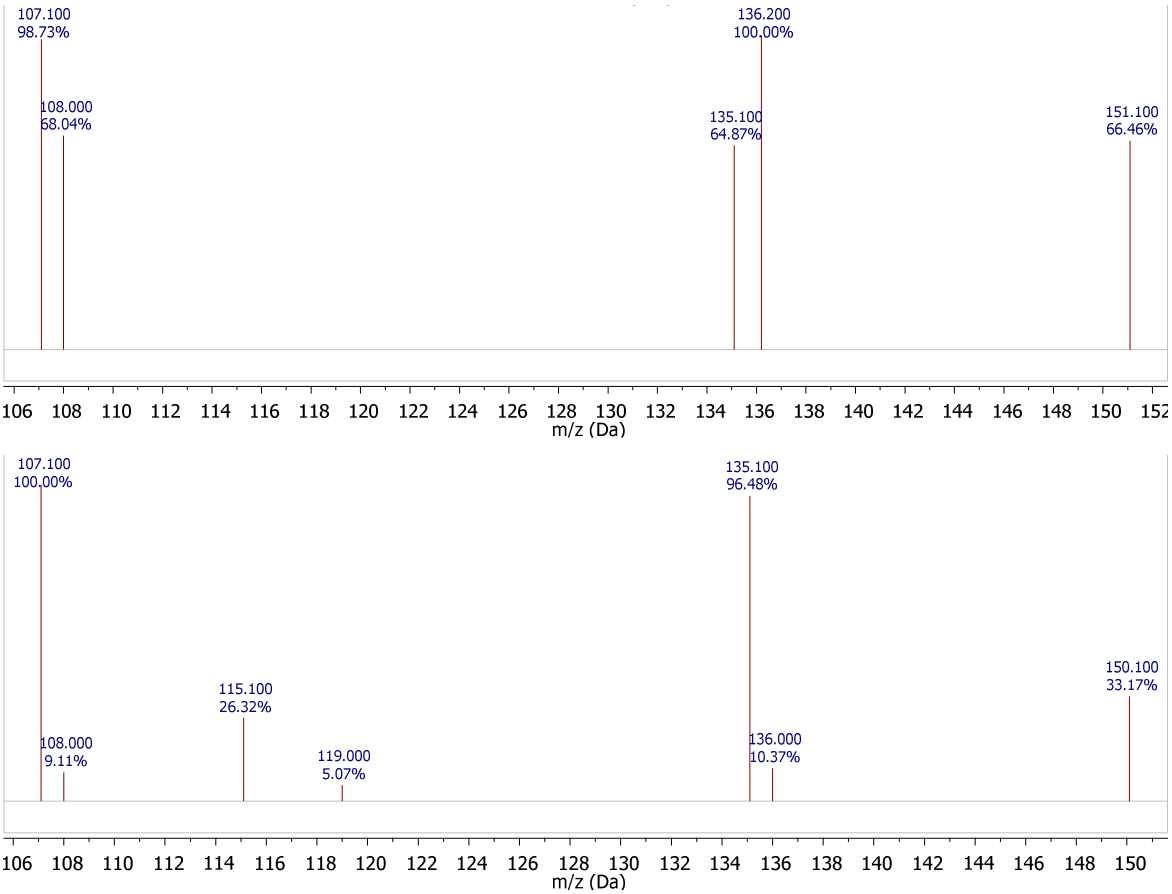


Figure S24. MS fragmentation for the thermolysis of **[2]ClO_4** in DMSO-d_6, with 10% D_2O (top) and MS of the product of the reaction in DMSO-d_6 in the absence of added D_2O (bottom). Formation of product in the absence of added D_2O is likely promoted by the trace water (~35 mM) present in the solvent.

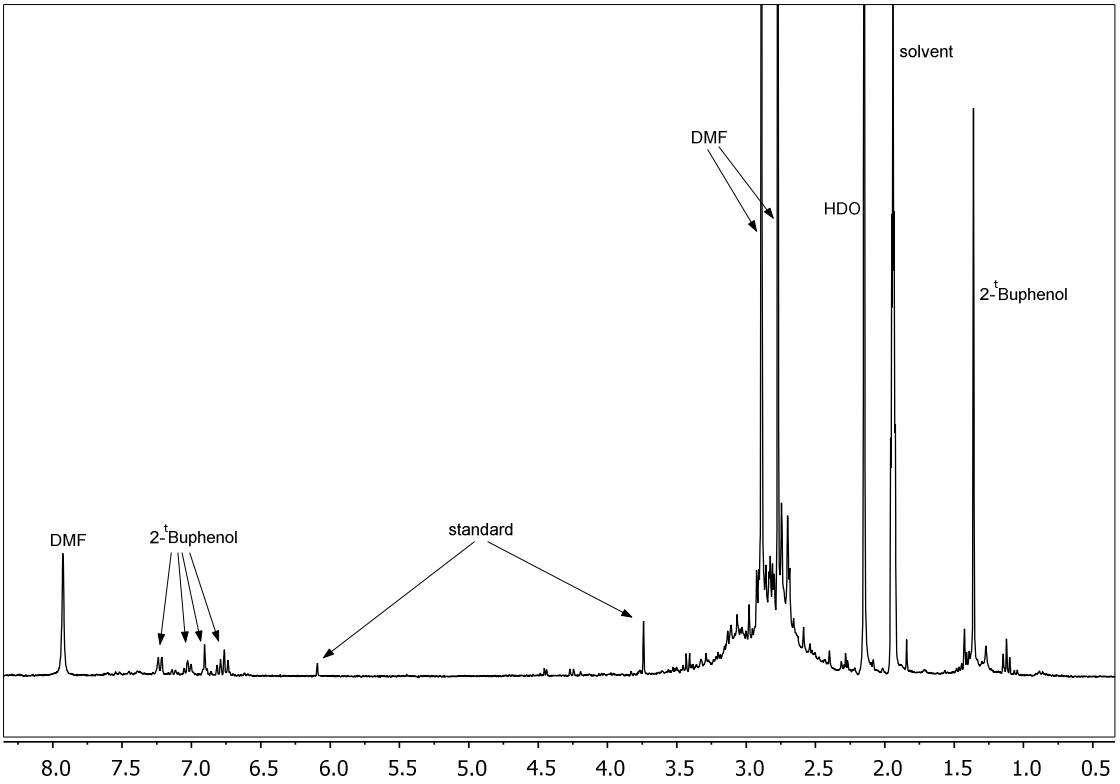
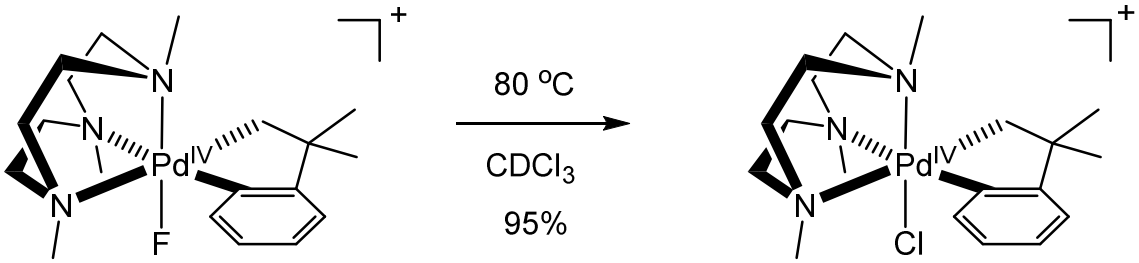


Figure S25. ^{1}H NMR of thermolysis of compound **[2]ClO$_4$** in DMF: heated at 110 ^{o}C for 4 hrs, then solvent was removed by vacuum distillation and residue was redissolved in CD_3CN.

Thermolysis of [(Me_3tacn)Pd^{IV}(F)($CH_2CMe_2C_6H_4$)]OTf ([5]OTf) in $CDCl_3$.

A stock solution of [**5]OTf** (6-10 mM) was prepared by dissolving [**5]OTf** in $CDCl_3$. 0.6 mL of the stock solution of [**5]OTf** was transferred into a NMR tube, followed by addition of 10 uL of a 1,3,5-trimethoxybenzene stock solution used as the internal standard. The solution was capped and sealed tight, before it was heated in the oil bath. The thermolysis process was periodically monitored by NMR, until the starting material was completely gone, and further heating does not induce any changes. The yields of the products were determined by NMR integration using 1,3,5-trimethoxybenzene as the internal standard, calculated as [moles of product]/[moles of **5**]*100%. Yield: 95%. ESI-MS (m/z): 446.1404; Calcd for [(Me_3tacn)Pd^{IV}(Cl)($CH_2CMe_2C_6H_4$)]$^+$: 446.1419. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.25 (d, 1H), 7.16 (t, J = 7.1 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 4.53 (d, J = 5.3 Hz, 2H), 4.01 (d,J = 5.3 Hz, 1H), 3.09 (s, 3H), 2.89 (s, 3H), 2.36 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H). The coupling constant for a doublet at 7.25 was not determined because of overlap with the solvent peak. The ESI-MS exhibits a peak at m/z 446.1404, which was identified as [(Me_3tacn)Pd^{IV}(Cl)($CH_2CMe_2C_6H_4$)]$^+$ (m/z 446.1419). The product was further confirmed by comparing to the independently synthesized authentic sample [(Me_3tacn)Pd^{IV}(Cl)($CH_2CMe_2C_6H_4$)](ClO_4) (see below).

Scheme S2. Thermolysis of [**5]OTf** in $CDCl_3$.



5 **6**

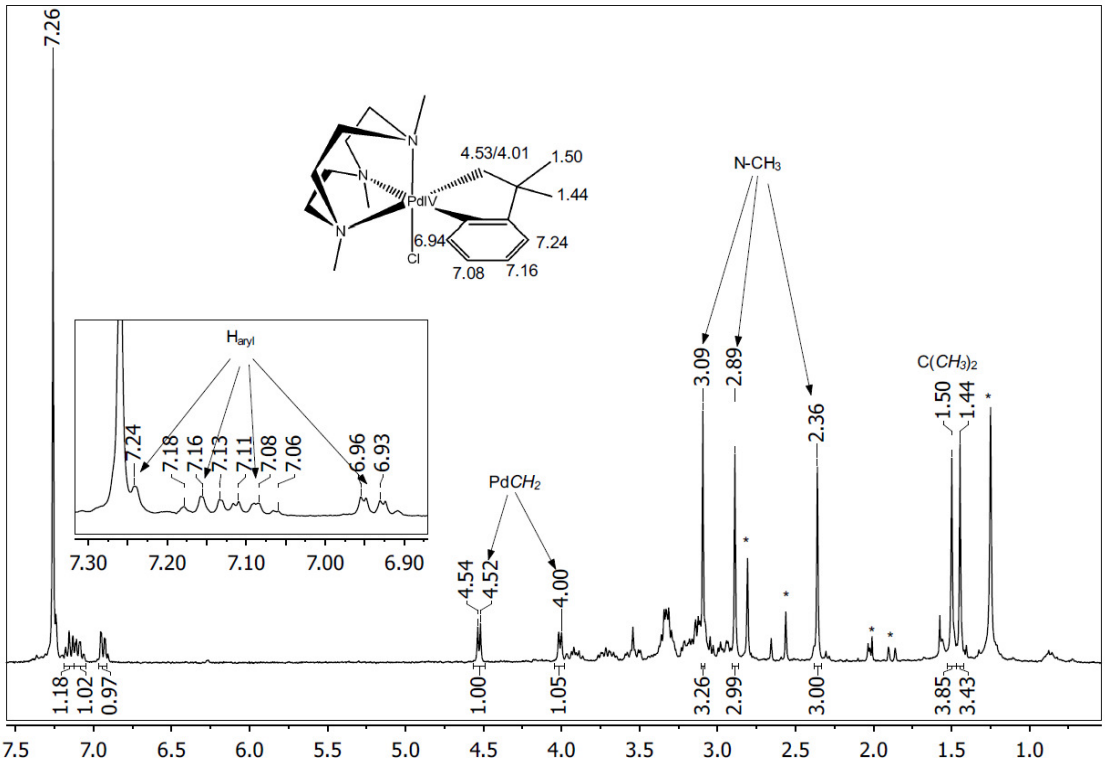


Figure S26. ^{1}H NMR of compound **[5]OTf** after heating at 80 ^{o}C in $CDCl_3$ for 9.5 h. Peaks labeled with asterisks are unidentified impurities.

Thermolysis of [(Me_3tacn)Pd^{IV}(Cl)($CH_2CMe_2C_6H_4$)]ClO_4 ([6]ClO_4) in DMSO.

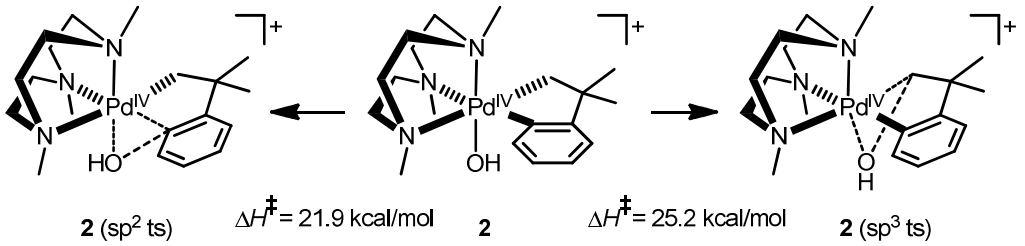
Compound **6** is very stable at RT. Unselective decomposition is also observed upon heating above 110 ^oC to give some unidentified products, which did not contain the expected C-Cl reductive elimination product according to GC-MS and NMR. The reaction solution was cooled down to RT. Then it was treated with 3 mL of $HClO_4$, followed by extraction with ether (3 x 1 mL). The ether layer were combined and washed with saturated aqueous $NaHCO_3$ solution, followed by washing with brine. The final ether solution was dried over K_2CO_3. Then 1 μL of the final solution was injected into GC-MS for analysis.

Thermolysis of [(Me_3tacn)Pd^{IV}(I)($CH_2CMe_2C_6H_4$)]I ([7]I) in DMSO.

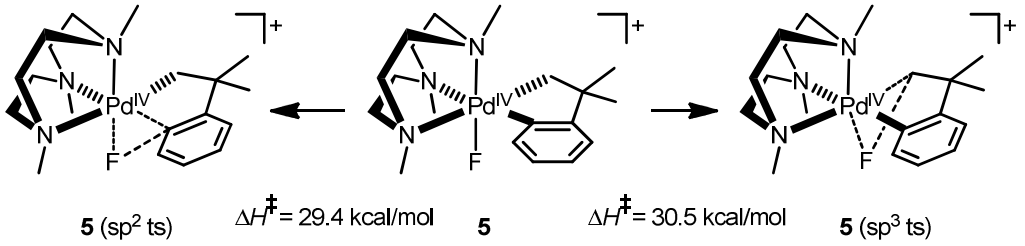
Compound **7** is very stable and no sign of decomposition was observed when heated below 100 ^oC over several hours. Unselective decomposition is observed upon heating above 110 ^oC to give unidentified products, which did not contain the expected C-I reductive elimination product according to GC-MS and NMR. GC-MS analysis was performed as follows. The reaction solution was cooled down to RT. Then it was treated with 3 mL of $HClO_4$, followed by extraction with ether (3 x 1 mL). The ether layer were combined and washed with saturated aqueous $NaHCO_3$ solution, followed by washing with brine. The final ether solution was dried over K_2CO_3. Then 1 μL of the final solution was injected into GC-MS for analysis.

VI. Computational details

The density functional theory (DFT) calculations were performed using the Gaussian 09 program package.[3] The M06 functional[4] along with the Stevens (CEP-31G)[5] valence basis sets and effective core potentials were employed. The CEP-31G valence basis set is valence triple-ζ for palladium and double-ζ for main group elements. The non-hydrogen main group elements were augmented with a d-polarization function: ξd = 0.8 for carbon, nitrogen, oxygen, and fluorine. This functional/basis set combination has been shown previously to reproduce well experimental parameters of organometallic complexes.[6] The optimized geometries were calculated without any symmetry constraints. The obtained minima were confirmed by the absence of any imaginary frequency, and the calculated transition states were checked by inspection of the single imaginary frequency along the reaction coordinate. Thermochemical data were calculated using default parameters at 298 K and 1 atm. Solvent corrections (DMSO) were performed using the SMD model.[7] The calculated energies of **2**, **5**, and the corresponding sp^2 and sp^3 transition states are shown below in kcal/mol (Figure S27), with the values for **2** and **5** being set to 0.0 as reference.



Complex	Enthalpy (kcal/mol)	Free Energy (kcal/mol)
2	0	0
2 (sp^2 ts)	**21.9**	**22.3**
2 (sp^3 ts)	**25.2**	**25.1**

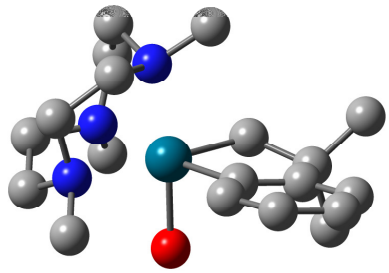


Complex	Enthalpy (kcal/mol)	Free Energy (kcal/mol)
5	0	0
5 (sp^2 ts)	**29.4**	**30.2**
5 (sp^3 ts)	**30.5**	**29.4**

Figure S27. Calculated transition state parameters for the C(sp^2)-X and C(sp^3)-X bond formation reactions from **2** and **5**.

Cartesian coordinates of the geometry optimized structures:

Complex **2**



Pd	8.69082100	3.31524300	7.33562600
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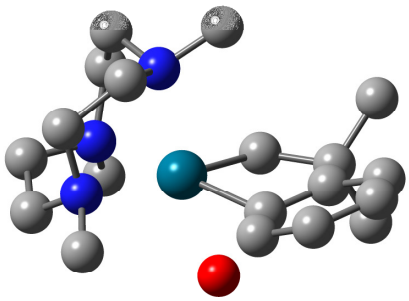
H	8.99933200	3.27797000	4.89076500
N	9.87323600	5.27844800	7.73132500
N	7.92848600	3.76729200	9.31370400
N	10.43667800	2.52437600	8.54676100
C	6.99812300	3.87913500	6.33848300
C	6.60320200	5.22609300	6.16295500
H	7.21093900	6.05039800	6.54978100
C	5.39125000	5.53207400	5.49032200
H	5.09447500	6.57978300	5.36087100
C	4.57438300	4.48799900	4.99239300
H	3.63962500	4.72155100	4.46930600
C	4.96700300	3.14052600	5.17354700
H	4.33033000	2.33217300	4.78858700
C	6.17663700	2.82489500	5.84950100
C	6.65895400	1.40229500	6.06881100
C	7.79098200	1.45369400	7.11768800
H	8.62925400	0.78016000	6.86438100
H	7.42026300	1.23455100	8.13615000
C	5.53538300	0.49360400	6.61836300
H	4.73145100	0.34846900	5.87191800
H	5.08483000	0.91880800	7.53598200
H	5.94478600	-0.50517100	6.86495100
C	7.16715900	0.80530500	4.73854800
H	8.01694900	1.38591200	4.33692000
H	6.36026900	0.79489100	3.98108200
H	7.50813700	-0.23691000	4.89213600
C	9.36608300	5.84660800	9.01961900
H	9.25964800	6.94355800	8.93911700
H	10.10043200	5.67073500	9.82406900
C	7.99408500	5.26996000	9.40056700
H	7.73425900	5.57751900	10.43362400
H	7.21506300	5.66252200	8.72361900
C	8.82568800	3.12931300	10.35978000
H	9.40262600	3.92239300	10.86128200
H	8.19496100	2.66907200	11.13895500
C	9.75387800	2.05284700	9.78375000
H	10.49677200	1.76408000	10.55627500

H	9.17583300	1.14996500	9.51880200
C	11.41034000	3.62640100	8.83614700
H	11.27366200	3.98193000	9.87046900
H	12.44300000	3.23655700	8.78022200
C	11.27139200	4.77453600	7.83908700
H	11.95251000	5.60122000	8.13313700
H	11.56170200	4.43135700	6.82927400
C	9.85623500	6.28452600	6.64638400
H	8.90767800	6.84284400	6.64785900
H	9.97658100	5.77408600	5.67436300
H	10.67900700	7.01755300	6.77973700
C	6.51742900	3.36427400	9.57753300
H	6.44266500	2.26541000	9.61027300
H	5.86018500	3.75649100	8.78383000
H	6.19426800	3.76753500	10.55684600
C	11.15297600	1.41035500	7.88511400
H	11.56292800	1.76959700	6.92623000
H	10.46252800	0.57469300	7.68651800
H	11.97814200	1.04433000	8.52929700

Complex **2**-sp^2-ts



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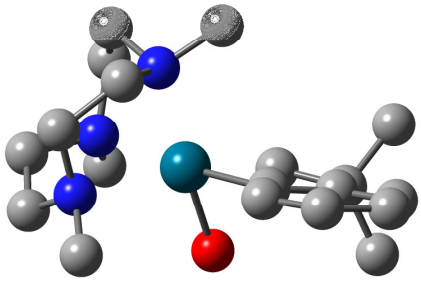
N	9.83443500	5.31441800	7.81437200
N	7.92112200	3.67526300	9.29848800
N	10.49380000	2.53295500	8.58900700
C	7.18061100	3.91315500	5.85424100
C	6.85400600	5.25743000	5.54566600
H	7.62435200	6.03286900	5.53617800
C	5.52027300	5.58425800	5.20342500
H	5.27044800	6.62870900	4.98050300
C	4.52663100	4.57500300	5.12693500
H	3.49587600	4.82797700	4.85448100
C	4.88387500	3.23169500	5.40013800
H	4.11906800	2.44540600	5.34395500
C	6.20765500	2.87353800	5.76685700
C	6.63902100	1.44333900	6.06915000
C	7.93547900	1.50226500	6.91971800
H	8.78399800	0.97838700	6.43315500
H	7.79429700	1.08927800	7.93554600
C	5.55133600	0.66121400	6.83638400
H	4.65333200	0.49779100	6.21175400
H	5.23990300	1.19047200	7.75611100
H	5.93984000	-0.33433100	7.12426200
C	6.90238300	0.69513900	4.73844300
H	7.69138500	1.17707900	4.12825500
H	5.98280100	0.66428500	4.12292900
H	7.22218600	-0.34557900	4.93807400
C	9.27524700	5.80086900	9.11860800
H	9.14885100	6.89795900	9.09175600
H	9.98649000	5.59805600	9.93626300
C	7.90795600	5.17190700	9.40479000
H	7.56184700	5.46599100	10.41779100
H	7.16675100	5.54030400	8.66976600
C	8.80053700	3.05620700	10.35276500
H	9.34060300	3.85567200	10.88544700
H	8.16704200	2.55829000	11.10775600
C	9.78790700	2.02350100	9.78411300
H	10.50012100	1.73810900	10.58892300
H	9.24300200	1.10928100	9.48441000

C	11.41576100	3.65795600	8.90425000
H	11.26602100	3.98771900	9.94629800
H	12.46886300	3.32122200	8.84514800
C	11.24401000	4.83145500	7.93448400
H	11.90160800	5.66861300	8.25425200
H	11.55863200	4.52439100	6.91810300
C	9.82504000	6.40919700	6.81843200
H	8.84119600	6.90536500	6.82196000
H	10.02878100	6.00046000	5.81298200
H	10.59385800	7.17008200	7.06754800
C	6.52845500	3.18622500	9.45306100
H	6.52283100	2.08358000	9.44530700
H	5.90710800	3.56439900	8.62056500
H	6.10535900	3.53822400	10.41558800
C	11.22507900	1.45425300	7.90289900
H	11.65445000	1.84430400	6.96126800
H	10.53953800	0.62411200	7.65988200
H	12.05036900	1.05610500	8.53236200

Complex **2**-sp^3-ts



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N	9.98519800	5.40981600	7.80836700
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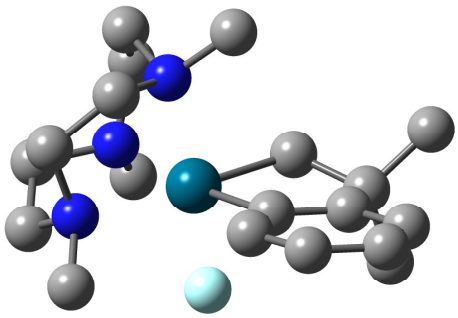
N	10.38291100	2.56023100	8.67166100
C	6.97066100	3.73138100	6.39880700
C	6.54481200	5.07911900	6.26339200
H	7.16102500	5.89620400	6.66124700
C	5.32459700	5.40425200	5.61840600
H	5.01698000	6.45328000	5.52960900
C	4.50962700	4.37063600	5.09377800
H	3.55971000	4.60874400	4.60094600
C	4.93852800	3.02691500	5.19197100
H	4.31634700	2.22960200	4.76232300
C	6.16742200	2.69641600	5.82953800
C	6.63972500	1.24207400	5.84251900
C	7.89332500	1.07706700	6.68393600
H	8.55912000	0.25733400	6.39269400
H	7.71948700	1.08881700	7.77585500
C	5.60452100	0.32059200	6.54469900
H	4.67489100	0.27425500	5.94824200
H	5.35321900	0.69308600	7.55490300
H	5.99690900	-0.71031400	6.63538400
C	6.85511400	0.72326000	4.40373900
H	7.55802000	1.34966100	3.82449000
H	5.89585700	0.71469900	3.85532300
H	7.24600600	-0.31151600	4.42437200
C	9.47343900	5.98722100	9.06612900
H	9.39333700	7.08973100	8.99405600
H	10.17926300	5.79589700	9.89406000
C	8.06888200	5.45321600	9.42484400
H	7.78973200	5.80146200	10.44164400
H	7.32076400	5.85318500	8.71741600
C	8.81953600	3.33584300	10.45295700
H	9.45527500	4.11622700	10.90168000
H	8.17347900	2.96086500	11.26630100
C	9.67170700	2.17940900	9.92484000

H	10.39288000	1.86312500	10.70848200
H	9.02708100	1.31297500	9.68644000
C	11.39831500	3.64026500	8.91240400
H	11.29100500	4.01948400	9.94266800
H	12.41351100	3.20563400	8.85392900
C	11.31752600	4.79028100	7.90151100
H	12.10227900	5.53687300	8.16915800
H	11.56636700	4.40392700	6.89222800
C	9.95116600	6.35579400	6.69047800
H	8.97474000	6.87021800	6.65410200
H	10.08881400	5.81084500	5.73577400
H	10.74507000	7.13402800	6.77069200
C	6.54406700	3.56975700	9.61799500
H	6.45690700	2.46937700	9.56777700
H	5.89109100	4.01806100	8.85115000
H	6.21514800	3.91250200	10.62018400
C	11.05729300	1.37425500	8.09675200
H	11.50380400	1.64698300	7.12571900
H	10.32450400	0.56656700	7.93356000
H	11.84995200	1.00466700	8.77989500

Complex **5**



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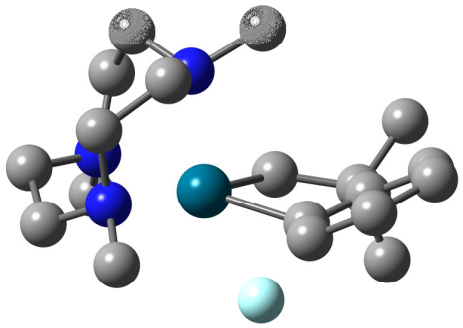
C	5.36393700	5.53515000	5.54315600
H	5.06567900	6.58221700	5.41310100
C	4.54879500	4.48876700	5.04863400
H	3.61117100	4.71992100	4.52989600
C	4.94682700	3.14206400	5.22364700
H	4.31405800	2.33237700	4.83558700
C	6.15908900	2.82842400	5.89545000
C	6.66266500	1.40948800	6.08577500
C	7.77430000	1.44992200	7.15258100
H	8.62623100	0.79123200	6.90276500
H	7.39709000	1.22065100	8.16503500
C	5.55450400	0.45824300	6.59089900
H	4.76611200	0.31702100	5.82762000
H	5.08159400	0.84593600	7.51370500
H	5.98518500	-0.53719200	6.81288700
C	7.20921900	0.87735400	4.74265100
H	8.02747600	1.51750300	4.36945200
H	6.40620900	0.85279800	3.98156700
H	7.59809800	-0.15209600	4.86598200
C	9.37415300	5.84894700	8.98511500
H	9.26266600	6.94312100	8.88191300
H	10.11135300	5.69314900	9.79060300
C	8.00336900	5.27874700	9.37716900
H	7.75796000	5.56926000	10.41732200
H	7.21615300	5.68105200	8.71792800
C	8.80646700	3.12130300	10.34084200
H	9.37120300	3.91600600	10.85218900
H	8.15680300	2.66129100	11.10327300
C	9.74346200	2.04635800	9.78161100
H	10.47608200	1.76767700	10.56709600
H	9.17447900	1.13903500	9.51381100

C	11.40602900	3.62365700	8.84946400
H	11.24554900	3.99524100	9.87435400
H	12.44043700	3.23628300	8.82178900
C	11.27961100	4.75292600	7.83017700
H	11.95771400	5.58490800	8.11342700
H	11.58029000	4.39213400	6.82915200
C	9.86776500	6.24747500	6.60392700
H	8.91580100	6.79919000	6.58971700
H	10.00001100	5.72751800	5.63916500
H	10.68552800	6.98550300	6.73631200
C	6.49835500	3.39203300	9.55117400
H	6.39830000	2.29573200	9.56774000
H	5.84182800	3.81677000	8.77558700
H	6.20658400	3.78869600	10.54167600
C	11.17497900	1.39824500	7.91656500
H	11.68095700	1.76426100	7.00773800
H	10.48256400	0.58603800	7.64176900
H	11.93590100	0.99446500	8.61503800
F	9.54265500	2.98653700	5.57499900

Complex **5**-sp^2-ts



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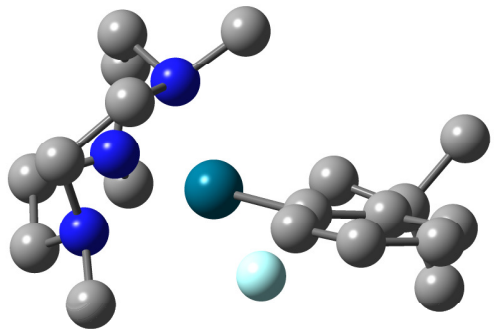
C	7.15766700	3.90432300	5.86452700
C	6.82857700	5.25391100	5.61980300
H	7.60178400	6.01854100	5.50912900
C	5.45592200	5.58995600	5.51525200
H	5.17782300	6.63945900	5.36348500
C	4.46251800	4.58082700	5.57212000
H	3.40288200	4.84214800	5.47786900
C	4.84601100	3.22452800	5.73426100
H	4.07333100	2.44602000	5.77565000
C	6.20800000	2.84840900	5.85206500
C	6.70695400	1.41851000	6.02993100
C	7.98398900	1.47747600	6.89962300
H	8.85359200	0.99142100	6.41110800
H	7.82881600	1.06641500	7.91436400
C	5.66197500	0.51715500	6.71832200
H	4.76703000	0.37690600	6.08380000
H	5.33851300	0.93063600	7.69248300
H	6.10002800	-0.48339000	6.89547800
C	7.01973800	0.81518400	4.64043100
H	7.79195400	1.39996300	4.11159400
H	6.10647400	0.79556200	4.01461700
H	7.38397500	-0.22477600	4.74950000
C	9.27643700	5.82227300	9.00672900
H	9.17078800	6.91978300	8.93654800
H	9.94613700	5.63634700	9.86271800
C	7.88473100	5.22923600	9.25573200
H	7.50068000	5.57609800	10.23795300
H	7.18572100	5.57859800	8.47143300
C	8.70082300	3.12738500	10.31098100
H	9.23335900	3.93312300	10.84173600
H	8.03464400	2.65707100	11.05545300
C	9.69088100	2.06191800	9.80753400
H	10.36902000	1.79266500	10.64607200
H	9.14133200	1.14724700	9.51820200
C	11.38419800	3.63743300	8.95237500

H	11.18780800	4.00253300	9.97435800
H	12.43101000	3.27863900	8.95671600
C	11.28053100	4.78101600	7.94142700
H	11.94083400	5.61545700	8.26261900
H	11.62981400	4.43424900	6.94918700
C	9.94381000	6.34127900	6.71338600
H	8.97010400	6.85052700	6.64084700
H	10.20201900	5.89848500	5.73529600
H	10.70764900	7.10213600	6.97794700
C	6.46194300	3.27095400	9.32625600
H	6.43352800	2.16851700	9.33699200
H	5.87767600	3.64502100	8.46597000
H	6.01033300	3.64975200	10.26538000
C	11.20806400	1.39660000	8.03098200
H	11.72281500	1.74474000	7.11763100
H	10.52101700	0.57666400	7.76034300
H	11.96575600	0.99921200	8.74054800
F	8.65934600	3.51618100	5.00184300

Complex **5**-sp^3-ts



Pd	8.63434000	3.21312900	7.47588300
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N	7.97442800	3.98519800	9.40100800
N	10.39985700	2.58604400	8.69284300
C	6.94570600	3.69993800	6.46593900
C	6.52014600	5.04830000	6.34262900
H	7.12766000	5.85823000	6.76591500
C	5.31565200	5.38850900	5.67601200
H	5.01370600	6.43999600	5.59851800
C	4.51198900	4.36604200	5.11626500
H	3.57383400	4.61146600	4.60512600
C	4.94066200	3.02164800	5.20215000
H	4.33103900	2.23369300	4.73955700
C	6.15450700	2.67577000	5.86066700
C	6.61165800	1.21579800	5.81223700
C	7.76750500	0.94518000	6.71723900
H	8.44082800	0.12095100	6.45720500
H	7.61191800	1.08057300	7.79928800
C	5.54263100	0.25262300	6.42325000
H	4.66006300	0.22742000	5.75898700
H	5.22090300	0.58419100	7.42679100
H	5.93134300	-0.78103500	6.49362300
C	6.91298200	0.77952800	4.36395900
H	7.67457500	1.43032400	3.90287700
H	5.99454100	0.82979700	3.75233200
H	7.27961400	-0.26431200	4.34678700
C	9.49133700	6.00772800	9.04132300
H	9.40451200	7.10841800	8.95251300
H	10.21039500	5.83369600	9.86174100
C	8.09355200	5.47870000	9.43585300
H	7.84244900	5.82982100	10.45841200
H	7.32716400	5.87822200	8.74951700
C	8.84633900	3.36846600	10.47675500
H	9.48342100	4.15536100	10.91179500
H	8.20591700	3.00038900	11.29714000
C	9.69707500	2.21080800	9.95178500
H	10.42300200	1.90184900	10.73397600
H	9.05478600	1.34080700	9.71908300
C	11.41251300	3.67176400	8.91454400

H	11.30384300	4.07347400	9.93581200
H	12.42904600	3.23921400	8.86558200
C	11.32069000	4.79375100	7.87413900
H	12.11093100	5.54639000	8.10595900
H	11.54907100	4.37377700	6.87297500
C	9.94328700	6.34756300	6.65721700
H	8.95767500	6.84284100	6.60669700
H	10.09880900	5.79550500	5.71028100
H	10.72218200	7.14099700	6.73673300
C	6.55912300	3.60394900	9.66723900
H	6.46738900	2.50366100	9.63351100
H	5.89862200	4.04510200	8.90335700
H	6.24900400	3.96276500	10.66936500
C	11.07587900	1.39434800	8.13072600
H	11.60001200	1.67364400	7.20132900
H	10.33342200	0.61130700	7.90325500
H	11.81557000	0.99112900	8.85366800
F	9.16616000	2.07534600	5.81123700

VII. X-ray structure determinations of 1 (LM15812), [2]ClO_4 (LM15612), [6]ClO_4 (LM5513), and [7]I (LM23312)

Crystals of appropriate dimension were mounted on a Mitgen cryoloops in a random orientation. Preliminary examination and data collection were performed using a Bruker Kappa Apex II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite monochromated Mo Kα radiation (λ= 0.71073 Å) from a fine focus sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of ϖ and ϕ scan frames with typical scan width of 0.5° and counting time of 15-30 seconds/frame at a crystal to detector distance of 3.5 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages[8] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of xyz centroids of reflections from the complete data set. Collected data were corrected for systematic errors using SADABS[8] based on the Laue symmetry using equivalent reflections.

Structure solution and refinement were carried out using the SHELXTL- PLUS software package[9]. The structures were solved by direct methods and refined successfully in the space group Cc in the case of (Me_3tacn)Pd($CH_2CMe_2C_6H_4$) (L15812), Pca21 for all other three cases. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms were treated using appropriate riding model (AFIX m3). The final residual values and structure refinement parameters are listed in Tables S1-S25.

Complete listings of positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms are listed in Tables S1-S8. Table of calculated and observed structure factors are available in electronic format.

Acknowledgement: Funding from the National Science Foundation (MRI, CHE-0420497) for the purchase of the ApexII diffractometer is acknowledged.

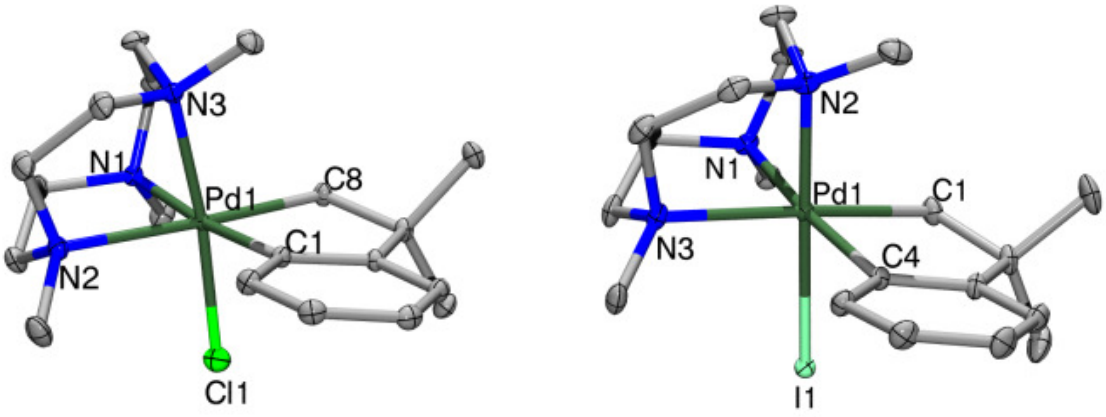


Figure S28. ORTEP representation of the cations of **6** (left) and **7** (right). Selected bond lengths (Å) and angels (°): **6**, Pd1-C1, 2.0170(19); Pd1-C8, 2.0592(19); Pd1-Cl1, 2.2490(7); Pd1-N1, 2.2144(17); Pd1-N2, 2.2651(17); Pd1-N3, 2.1035(19); Cl1-Pd1-C1, 87.02(6); Cl1-Pd1-C8, 88.60(6); C1-Pd1-C8, 81.36(7); **7**, Pd1-C1, 2.0610(15); Pd1-C4, 2.0207(15); Pd1- I1, 2.5902(3); Pd1-N1, 2.2287(14); Pd1-N2, 2.1944(14); Pd1-N3, 2.2983(13); I1-Pd1-C1, 88.48(5); I1-Pd1-C4, 81.42(6); C1-Pd1-C4, 81.42(6).

Table S1. Crystal data and structure refinement for lm15812.

Identification code	l15812/lt/Fengrui/Me3tacnPdII	
Empirical formula	C_{19} H_{33} N_3 Pd	
Formula weight	409.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 12.010(5) Å	α = 90°.
	b = 14.065(5) Å	□β = 113.96(2)°.
	c = 12.461(5) Å	□γ = 90°.
Volume	1923.6(13) $Å^3$	
Z	4	
Density (calculated)	1.415 Mg/m^3	
Absorption coefficient	0.969 mm^{-1}	
F(000)	856	
Crystal size	0.22 x 0.13 x 0.05 mm^3	
Theta range for data collection	2.35 to 26.85°.	
Index ranges	-15≤h≤15, -17≤k≤17, -15≤l≤15	
Reflections collected	16565	
Independent reflections	4071 [R(int) = 0.0592]	
Completeness to theta = 26.85°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9523 and 0.8130	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4071 / 2 / 213	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0525	
R indices (all data)	R1 = 0.0299, wR2 = 0.0542	
Absolute structure parameter	0.00(2)	
Largest diff. peak and hole	0.321 and -0.341 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for lm15812.

Pd(1)-C(8)	2.010(6)
Pd(1)-C(1)	2.015(3)
Pd(1)-N(1)	2.215(4)
Pd(1)-N(3)	2.240(3)
N(1)-C(17)	1.498(4)
N(1)-C(15)	1.500(5)
N(1)-C(11)	1.501(5)
N(2)-C(18)	1.438(4)
N(2)-C(13)	1.444(4)
N(2)-C(12)	1.469(4)
N(3)-C(19)	1.476(4)
N(3)-C(16)	1.484(4)
N(3)-C(14)	1.488(4)
C(1)-C(6)	1.396(4)
C(1)-C(2)	1.405(4)
C(2)-C(3)	1.394(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.367(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.398(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.400(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.530(4)
C(7)-C(9)	1.522(4)
C(7)-C(10)	1.531(5)
C(7)-C(8)	1.542(5)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.537(5)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.542(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.510(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800

C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(8)-Pd(1)-C(1)	78.99(14)
C(8)-Pd(1)-N(1)	176.5(2)
C(1)-Pd(1)-N(1)	102.80(12)
C(8)-Pd(1)-N(3)	97.22(12)
C(1)-Pd(1)-N(3)	175.42(11)
N(1)-Pd(1)-N(3)	81.12(10)
C(17)-N(1)-C(15)	106.0(3)
C(17)-N(1)-C(11)	109.1(3)
C(15)-N(1)-C(11)	112.7(3)
C(17)-N(1)-Pd(1)	113.8(3)
C(15)-N(1)-Pd(1)	101.0(2)
C(11)-N(1)-Pd(1)	113.9(3)
C(18)-N(2)-C(13)	115.8(3)
C(18)-N(2)-C(12)	116.2(3)
C(13)-N(2)-C(12)	117.5(3)
C(19)-N(3)-C(16)	108.1(3)
C(19)-N(3)-C(14)	109.3(3)
C(16)-N(3)-C(14)	110.4(2)
C(19)-N(3)-Pd(1)	111.2(2)
C(16)-N(3)-Pd(1)	108.21(18)
C(14)-N(3)-Pd(1)	109.58(19)
C(6)-C(1)-C(2)	117.1(3)
C(6)-C(1)-Pd(1)	116.1(2)
C(2)-C(1)-Pd(1)	126.6(2)
C(3)-C(2)-C(1)	121.4(3)
C(3)-C(2)-H(2)	119.3
C(1)-C(2)-H(2)	119.3
C(4)-C(3)-C(2)	120.6(3)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	119.5(3)
C(3)-C(4)-H(4)	120.2
C(5)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	119.9(3)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(1)-C(6)-C(5)	121.3(3)
C(1)-C(6)-C(7)	114.1(3)
C(5)-C(6)-C(7)	124.6(3)
C(9)-C(7)-C(6)	112.1(3)
C(9)-C(7)-C(10)	109.5(3)
C(6)-C(7)-C(10)	109.9(3)
C(9)-C(7)-C(8)	111.5(3)
C(6)-C(7)-C(8)	104.1(3)
C(10)-C(7)-C(8)	109.6(3)
C(7)-C(8)-Pd(1)	110.9(3)
C(7)-C(8)-H(8A)	109.5
Pd(1)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5

Pd(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	108.1
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-C(12)	116.4(3)
N(1)-C(11)-H(11A)	108.2
C(12)-C(11)-H(11A)	108.2
N(1)-C(11)-H(11B)	108.2
C(12)-C(11)-H(11B)	108.2
H(11A)-C(11)-H(11B)	107.3
N(2)-C(12)-C(11)	115.8(3)
N(2)-C(12)-H(12A)	108.3
C(11)-C(12)-H(12A)	108.3
N(2)-C(12)-H(12B)	108.3
C(11)-C(12)-H(12B)	108.3
H(12A)-C(12)-H(12B)	107.4
N(2)-C(13)-C(14)	113.9(3)
N(2)-C(13)-H(13A)	108.8
C(14)-C(13)-H(13A)	108.8
N(2)-C(13)-H(13B)	108.8
C(14)-C(13)-H(13B)	108.8
H(13A)-C(13)-H(13B)	107.7
N(3)-C(14)-C(13)	112.7(3)
N(3)-C(14)-H(14A)	109.0
C(13)-C(14)-H(14A)	109.0
N(3)-C(14)-H(14B)	109.0
C(13)-C(14)-H(14B)	109.0
H(14A)-C(14)-H(14B)	107.8
N(1)-C(15)-C(16)	111.6(3)
N(1)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15A)	109.3
N(1)-C(15)-H(15B)	109.3
C(16)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
N(3)-C(16)-C(15)	110.5(2)
N(3)-C(16)-H(16A)	109.6
C(15)-C(16)-H(16A)	109.6
N(3)-C(16)-H(16B)	109.6
C(15)-C(16)-H(16B)	109.6
H(16A)-C(16)-H(16B)	108.1
N(1)-C(17)-H(17A)	109.5
N(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

N(2)-C(18)-H(18A)	109.5
N(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(3)-C(19)-H(19A)	109.5
N(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Projection view with 50% thermal ellipsoids:

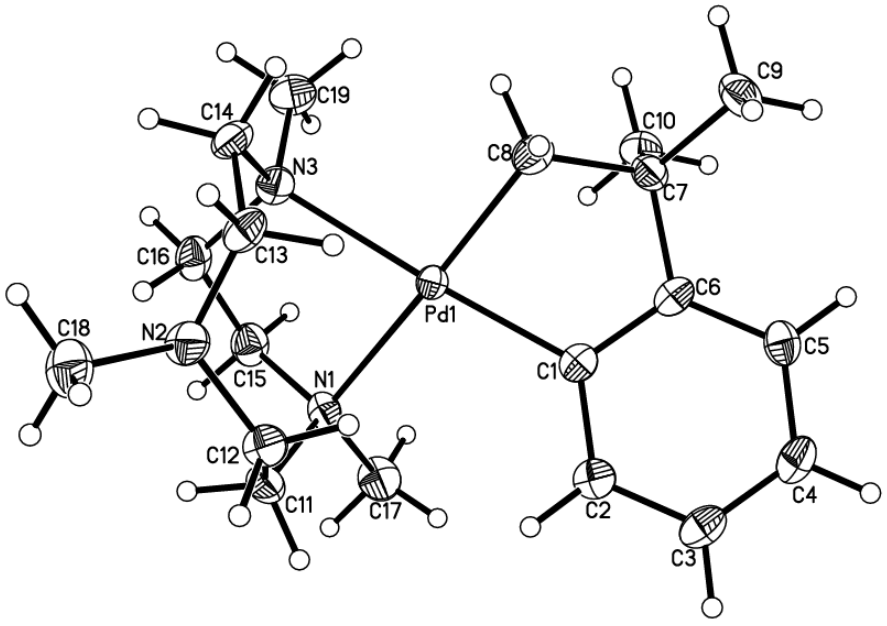


Table S3. Crystal data and structure refinement for lm15612.

Identification code	l15612/lt/Fengrui/Me3tacnPdIV(OH)	
Empirical formula	C_{19} H_{34} Cl N_3 O_5 Pd	
Formula weight	526.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 16.768(5) Å	α = 90°.
	b = 8.477(2) Å	β = 90°.
	c = 14.704(4) Å	γ = 90°.
Volume	2090.1(10) $Å^3$	
Z	4	
Density (calculated)	1.673 Mg/m^3	
Absorption coefficient	1.052 mm^{-1}	
F(000)	1088	
Crystal size	0.18 x 0.15 x 0.14 mm^3	
Theta range for data collection	2.40 to 27.58°.	
Index ranges	-21≤h≤21, -10≤k≤10, -19≤l≤19	
Reflections collected	54583	
Independent reflections	4780 [R(int) = 0.0682]	
Completeness to theta = 27.58°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8675 and 0.8324	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4780 / 1 / 268	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0482	
R indices (all data)	R1 = 0.0247, wR2 = 0.0498	
Absolute structure parameter	-0.005(18)	
Largest diff. peak and hole	0.273 and -0.516 e.$Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for lm15612.

Pd(1)-O(1)	2.0185(17)
Pd(1)-C(1)	2.024(2)
Pd(1)-C(8)	2.061(2)
Pd(1)-N(2)	2.117(2)
Pd(1)-N(3)	2.227(2)
Pd(1)-N(1)	2.263(2)
Cl(1)-O(4)	1.432(2)
Cl(1)-O(2)	1.435(2)
Cl(1)-O(5)	1.436(2)
Cl(1)-O(3)	1.444(2)
O(1)-H(1)	0.8400
N(1)-C(17)	1.481(3)
N(1)-C(11)	1.484(3)
N(1)-C(16)	1.490(3)
N(2)-C(18)	1.488(3)
N(2)-C(12)	1.505(3)
N(2)-C(13)	1.512(3)
N(3)-C(19)	1.478(3)
N(3)-C(14)	1.488(3)
N(3)-C(15)	1.501(3)
C(1)-C(2)	1.399(3)
C(1)-C(6)	1.413(3)
C(2)-C(3)	1.388(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.388(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.399(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.402(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.512(3)
C(7)-C(8)	1.533(3)
C(7)-C(10)	1.538(3)
C(7)-C(9)	1.547(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.530(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.505(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.492(4)

C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

O(1)-Pd(1)-C(1)	87.29(9)
O(1)-Pd(1)-C(8)	90.02(8)
C(1)-Pd(1)-C(8)	81.36(9)
O(1)-Pd(1)-N(2)	171.73(8)
C(1)-Pd(1)-N(2)	95.18(9)
C(8)-Pd(1)-N(2)	98.15(9)
O(1)-Pd(1)-N(3)	95.83(7)
C(1)-Pd(1)-N(3)	173.45(8)
C(8)-Pd(1)-N(3)	92.85(8)
N(2)-Pd(1)-N(3)	82.54(8)
O(1)-Pd(1)-N(1)	89.37(7)
C(1)-Pd(1)-N(1)	105.25(9)
C(8)-Pd(1)-N(1)	173.32(8)
N(2)-Pd(1)-N(1)	82.37(8)
N(3)-Pd(1)-N(1)	80.60(7)
O(4)-Cl(1)-O(2)	110.34(12)
O(4)-Cl(1)-O(5)	109.24(15)
O(2)-Cl(1)-O(5)	110.70(14)
O(4)-Cl(1)-O(3)	109.25(14)
O(2)-Cl(1)-O(3)	108.86(14)
O(5)-Cl(1)-O(3)	108.41(15)
Pd(1)-O(1)-H(1)	109.5
C(17)-N(1)-C(11)	112.32(19)
C(17)-N(1)-C(16)	106.3(2)
C(11)-N(1)-C(16)	112.3(2)
C(17)-N(1)-Pd(1)	116.08(15)
C(11)-N(1)-Pd(1)	107.64(15)
C(16)-N(1)-Pd(1)	101.78(14)
C(18)-N(2)-C(12)	106.7(2)
C(18)-N(2)-C(13)	109.4(2)
C(12)-N(2)-C(13)	110.6(2)
C(18)-N(2)-Pd(1)	115.94(16)
C(12)-N(2)-Pd(1)	104.49(16)
C(13)-N(2)-Pd(1)	109.51(15)
C(19)-N(3)-C(14)	109.86(19)
C(19)-N(3)-C(15)	109.04(19)
C(14)-N(3)-C(15)	110.99(19)
C(19)-N(3)-Pd(1)	115.67(15)
C(14)-N(3)-Pd(1)	101.74(14)
C(15)-N(3)-Pd(1)	109.39(15)
C(2)-C(1)-C(6)	119.3(2)
C(2)-C(1)-Pd(1)	124.96(18)

C(6)-C(1)-Pd(1)	115.74(17)
C(3)-C(2)-C(1)	120.5(2)
C(3)-C(2)-H(2)	119.7
C(1)-C(2)-H(2)	119.7
C(4)-C(3)-C(2)	120.8(2)
C(4)-C(3)-H(3)	119.6
C(2)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	119.4(2)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	120.7(2)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	119.4(2)
C(5)-C(6)-C(7)	122.7(2)
C(1)-C(6)-C(7)	117.9(2)
C(6)-C(7)-C(8)	108.26(19)
C(6)-C(7)-C(10)	111.0(2)
C(8)-C(7)-C(10)	110.2(2)
C(6)-C(7)-C(9)	109.4(2)
C(8)-C(7)-C(9)	109.32(19)
C(10)-C(7)-C(9)	108.6(2)
C(7)-C(8)-Pd(1)	114.92(16)
C(7)-C(8)-H(8A)	108.5
Pd(1)-C(8)-H(8A)	108.5
C(7)-C(8)-H(8B)	108.5
Pd(1)-C(8)-H(8B)	108.5
H(8A)-C(8)-H(8B)	107.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-C(12)	112.0(2)
N(1)-C(11)-H(11A)	109.2
C(12)-C(11)-H(11A)	109.2
N(1)-C(11)-H(11B)	109.2
C(12)-C(11)-H(11B)	109.2
H(11A)-C(11)-H(11B)	107.9
N(2)-C(12)-C(11)	113.3(2)
N(2)-C(12)-H(12A)	108.9
C(11)-C(12)-H(12A)	108.9
N(2)-C(12)-H(12B)	108.9
C(11)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.7
C(14)-C(13)-N(2)	113.2(2)
C(14)-C(13)-H(13A)	108.9
N(2)-C(13)-H(13A)	108.9
C(14)-C(13)-H(13B)	108.9

N(2)-C(13)-H(13B)	108.9
H(13A)-C(13)-H(13B)	107.7
N(3)-C(14)-C(13)	111.4(2)
N(3)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14A)	109.3
N(3)-C(14)-H(14B)	109.3
C(13)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108.0
C(16)-C(15)-N(3)	111.5(2)
C(16)-C(15)-H(15A)	109.3
N(3)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15B)	109.3
N(3)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
N(1)-C(16)-C(15)	113.6(2)
N(1)-C(16)-H(16A)	108.9
C(15)-C(16)-H(16A)	108.9
N(1)-C(16)-H(16B)	108.9
C(15)-C(16)-H(16B)	108.9
H(16A)-C(16)-H(16B)	107.7
N(1)-C(17)-H(17A)	109.5
N(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(2)-C(18)-H(18A)	109.5
N(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(3)-C(19)-H(19A)	109.5
N(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Projection view with 50% thermal ellipsoids:

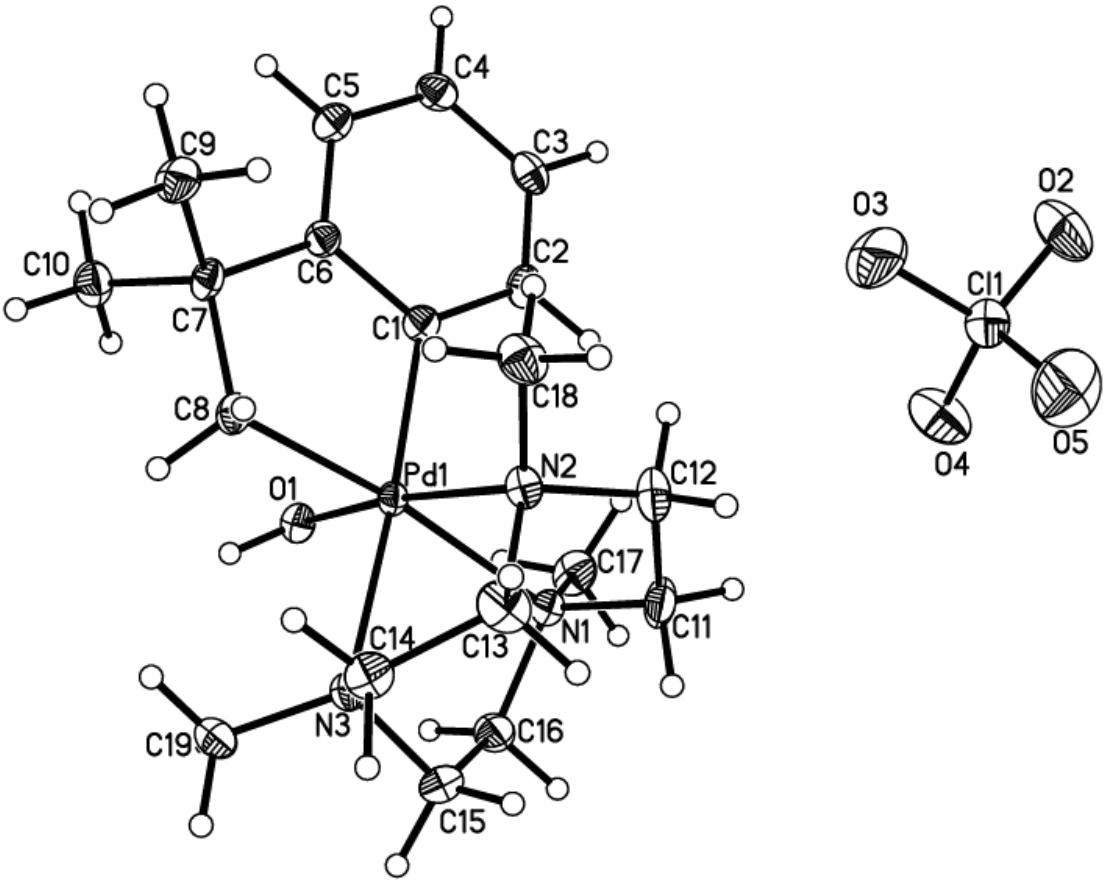


Table S5. Crystal data and structure refinement for lm5513.

Identification code	l5513/lt/Fengrui	
Empirical formula	C19 H33 Cl2 N3 O4 Pd	
Formula weight	544.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c a 2_1	
Unit cell dimensions	a = 16.5967(7) Å	□α = 90°.
	b = 8.3780(4) Å	□β = 90°.
	c = 15.0330(6) Å	□ γ = 90°.
Volume	2090.30(16) $Å^3$	
Z	4	
Density (calculated)	1.731 Mg/m^3	
Absorption coefficient	1.176 mm^{-1}	
F(000)	1120	
Crystal size	0.258 x 0.257 x 0.251 mm^3	
Theta range for data collection	2.431 to 38.999°.	
Index ranges	-29≤h≤29, -14≤k≤14, -24≤l≤26	
Reflections collected	79064	
Independent reflections	11727 [R(int) = 0.0439]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8032 and 0.7252	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11727 / 24 / 295	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0264, wR2 = 0.0597	
R indices (all data)	R1 = 0.0307, wR2 = 0.0613	
Absolute structure parameter	-0.002(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.843 and -1.100 $e.Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for lm5513.

Pd(1)-C(1)	2.0170(19)
Pd(1)-C(8)	2.0592(19)
Pd(1)-N(3)	2.1035(19)
Pd(1)-N(1)	2.2144(17)
Pd(1)-Cl(1)	2.2490(7)
Pd(1)-Cl(1')	2.249(6)
Pd(1)-N(2)	2.2651(17)
N(1)-C(17)	1.479(3)
N(1)-C(11)	1.489(3)
N(1)-C(16)	1.491(3)
N(2)-C(18)	1.483(3)
N(2)-C(15)	1.486(3)
N(2)-C(14)	1.489(3)
N(3)-C(19)	1.488(3)
N(3)-C(13)	1.502(3)
N(3)-C(12)	1.510(3)
C(1)-C(2)	1.395(3)
C(1)-C(6)	1.401(3)
C(2)-C(3)	1.392(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.386(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.386(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.398(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.507(3)
C(7)-C(8)	1.534(3)
C(7)-C(9)	1.537(3)
C(7)-C(10)	1.542(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.515(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.517(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.506(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900

C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
Cl(2)-O(3)	1.430(6)
Cl(2)-O(4)	1.442(5)
Cl(2)-O(2)	1.442(3)
Cl(2)-O(1)	1.457(4)
Cl(2')-O(1)	1.329(17)
Cl(2')-O(2)	1.347(15)
Cl(2')-O(4')	1.490(18)
Cl(2')-O(3')	1.68(3)

C(1)-Pd(1)-C(8)	81.36(7)
C(1)-Pd(1)-N(3)	95.16(8)
C(8)-Pd(1)-N(3)	97.65(8)
C(1)-Pd(1)-N(1)	173.35(7)
C(8)-Pd(1)-N(1)	92.71(7)
N(3)-Pd(1)-N(1)	82.59(7)
C(1)-Pd(1)-Cl(1)	87.02(6)
C(8)-Pd(1)-Cl(1)	88.60(6)
N(3)-Pd(1)-Cl(1)	173.62(5)
N(1)-Pd(1)-Cl(1)	95.89(5)
C(1)-Pd(1)-Cl(1')	91.9(4)
C(8)-Pd(1)-Cl(1')	110.1(4)
N(3)-Pd(1)-Cl(1')	152.1(4)
N(1)-Pd(1)-Cl(1')	93.0(4)
C(1)-Pd(1)-N(2)	105.87(7)
C(8)-Pd(1)-N(2)	172.75(7)
N(3)-Pd(1)-N(2)	82.34(7)
N(1)-Pd(1)-N(2)	80.09(6)
Cl(1)-Pd(1)-N(2)	91.31(5)
Cl(1')-Pd(1)-N(2)	69.8(4)
C(17)-N(1)-C(11)	110.33(17)
C(17)-N(1)-C(16)	109.25(16)
C(11)-N(1)-C(16)	110.18(17)
C(17)-N(1)-Pd(1)	114.68(13)
C(11)-N(1)-Pd(1)	102.00(12)
C(16)-N(1)-Pd(1)	110.19(12)
C(18)-N(2)-C(15)	106.19(18)
C(18)-N(2)-C(14)	112.09(18)
C(15)-N(2)-C(14)	112.04(19)
C(18)-N(2)-Pd(1)	116.68(15)
C(15)-N(2)-Pd(1)	102.50(12)
C(14)-N(2)-Pd(1)	107.02(13)
C(19)-N(3)-C(13)	107.15(17)
C(19)-N(3)-C(12)	108.94(18)
C(13)-N(3)-C(12)	110.90(18)
C(19)-N(3)-Pd(1)	115.51(15)
C(13)-N(3)-Pd(1)	104.22(14)
C(12)-N(3)-Pd(1)	110.00(13)

C(2)-C(1)-C(6)	119.49(18)
C(2)-C(1)-Pd(1)	124.59(15)
C(6)-C(1)-Pd(1)	115.87(13)
C(3)-C(2)-C(1)	120.42(19)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	120.04(18)
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(3)-C(4)-C(5)	119.99(19)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	120.55(19)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	119.48(18)
C(5)-C(6)-C(7)	122.22(17)
C(1)-C(6)-C(7)	118.27(17)
C(6)-C(7)-C(8)	108.03(16)
C(6)-C(7)-C(9)	110.57(18)
C(8)-C(7)-C(9)	110.93(16)
C(6)-C(7)-C(10)	110.27(16)
C(8)-C(7)-C(10)	108.27(17)
C(9)-C(7)-C(10)	108.75(17)
C(7)-C(8)-Pd(1)	114.70(13)
C(7)-C(8)-H(8A)	108.6
Pd(1)-C(8)-H(8A)	108.6
C(7)-C(8)-H(8B)	108.6
Pd(1)-C(8)-H(8B)	108.6
H(8A)-C(8)-H(8B)	107.6
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-C(12)	110.88(17)
N(1)-C(11)-H(11A)	109.5
C(12)-C(11)-H(11A)	109.5
N(1)-C(11)-H(11B)	109.5
C(12)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
N(3)-C(12)-C(11)	112.75(19)
N(3)-C(12)-H(12A)	109.0
C(11)-C(12)-H(12A)	109.0
N(3)-C(12)-H(12B)	109.0
C(11)-C(12)-H(12B)	109.0
H(12A)-C(12)-H(12B)	107.8
N(3)-C(13)-C(14)	112.99(18)
N(3)-C(13)-H(13A)	109.0

C(14)-C(13)-H(13A)	109.0
N(3)-C(13)-H(13B)	109.0
C(14)-C(13)-H(13B)	109.0
H(13A)-C(13)-H(13B)	107.8
N(2)-C(14)-C(13)	111.64(18)
N(2)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14A)	109.3
N(2)-C(14)-H(14B)	109.3
C(13)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108.0
N(2)-C(15)-C(16)	112.24(18)
N(2)-C(15)-H(15A)	109.2
C(16)-C(15)-H(15A)	109.2
N(2)-C(15)-H(15B)	109.2
C(16)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
N(1)-C(16)-C(15)	111.21(18)
N(1)-C(16)-H(16A)	109.4
C(15)-C(16)-H(16A)	109.4
N(1)-C(16)-H(16B)	109.4
C(15)-C(16)-H(16B)	109.4
H(16A)-C(16)-H(16B)	108.0
N(1)-C(17)-H(17A)	109.5
N(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(2)-C(18)-H(18A)	109.5
N(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(3)-C(19)-H(19A)	109.5
N(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(3)-Cl(2)-O(4)	115.6(19)
O(3)-Cl(2)-O(2)	110.6(7)
O(4)-Cl(2)-O(2)	104.1(11)
O(3)-Cl(2)-O(1)	111.2(7)
O(4)-Cl(2)-O(1)	107.1(6)
O(2)-Cl(2)-O(1)	107.6(3)
O(1)-Cl(2')-O(2)	121.9(16)
O(1)-Cl(2')-O(4')	114.4(12)
O(2)-Cl(2')-O(4')	117.4(12)
O(1)-Cl(2')-O(3')	101.1(15)
O(2)-Cl(2')-O(3')	98.5(15)
O(4')-Cl(2')-O(3')	95.3(18)

Projection view with 50% probability ellipsoids:

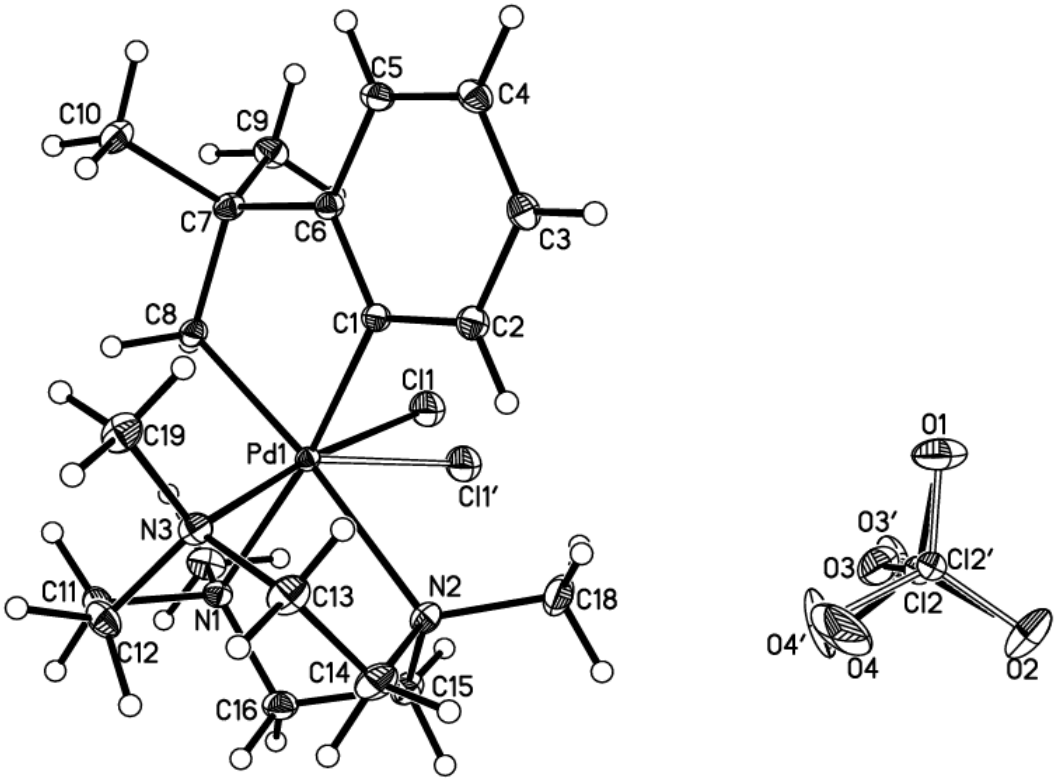


Table S7. Crystal data and structure refinement for lm23312.

Identification code	l23312/lt/Fengrui/Me3tacnPd(IV)	
Empirical formula	C_{19} H_{33} I_2 N_3 Pd	
Formula weight	663.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 16.110(2) Å	α = 90°.
	b = 8.7912(14) Å	β = 90°.
	c = 15.537(2) Å	γ = 90°.
Volume	2200.3(6) $Å^3$	
Z	4	
Density (calculated)	2.003 Mg/m^3	
Absorption coefficient	3.657 mm^{-1}	
F(000)	1280	
Crystal size	0.38 x 0.16 x 0.14 mm^3	
Theta range for data collection	2.32 to 39.06°.	
Index ranges	-28≤h≤28, -15≤k≤15, -27≤l≤27	
Reflections collected	159143	
Independent reflections	12564 [R(int) = 0.0409]	
Completeness to theta = 39.06°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6304 and 0.3363	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12564 / 10 / 238	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0196, wR2 = 0.0385	
R indices (all data)	R1 = 0.0218, wR2 = 0.0391	
Absolute structure parameter	-0.010(8)	
Largest diff. peak and hole	1.407 and -0.690 $e.Å^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for lm23312.

Pd(1)-C(4)	2.0207(15)
Pd(1)-C(1)	2.0610(15)
Pd(1)-N(2)	2.1944(14)
Pd(1)-N(1)	2.2287(14)
Pd(1)-N(3)	2.2983(13)
Pd(1)-I(1)	2.5902(3)
Pd(1')-C(4)	1.930(6)
Pd(1')-N(2)	1.970(8)
Pd(1')-C(1)	2.197(6)
Pd(1')-N(3)	2.200(6)
Pd(1')-N(1)	2.339(7)
Pd(1')-I(1')	2.565(4)
N(1)-C(15)	1.4821(19)
N(1)-C(9)	1.485(2)
N(1)-C(14)	1.487(2)
N(2)-C(16)	1.478(2)
N(2)-C(11)	1.493(2)
N(2)-C(10)	1.507(2)
C(3)-C(8)	1.398(2)
C(3)-C(4)	1.402(2)
C(3)-C(2)	1.504(2)
N(3)-C(17)	1.479(2)
N(3)-C(13)	1.490(2)
N(3)-C(12)	1.497(2)
C(4)-C(5)	1.393(2)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(5)-C(6)	1.393(2)
C(5)-H(5)	0.9500
C(1)-C(2)	1.531(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(14)-C(13)	1.509(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(2)-C(19)	1.539(2)
C(2)-C(18)	1.541(2)
C(11)-C(12)	1.516(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(9)-C(10)	1.514(2)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(8)-C(7)	1.392(2)
C(8)-H(8)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(6)-C(7)	1.383(2)
C(6)-H(6)	0.9500
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(7)-H(7)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

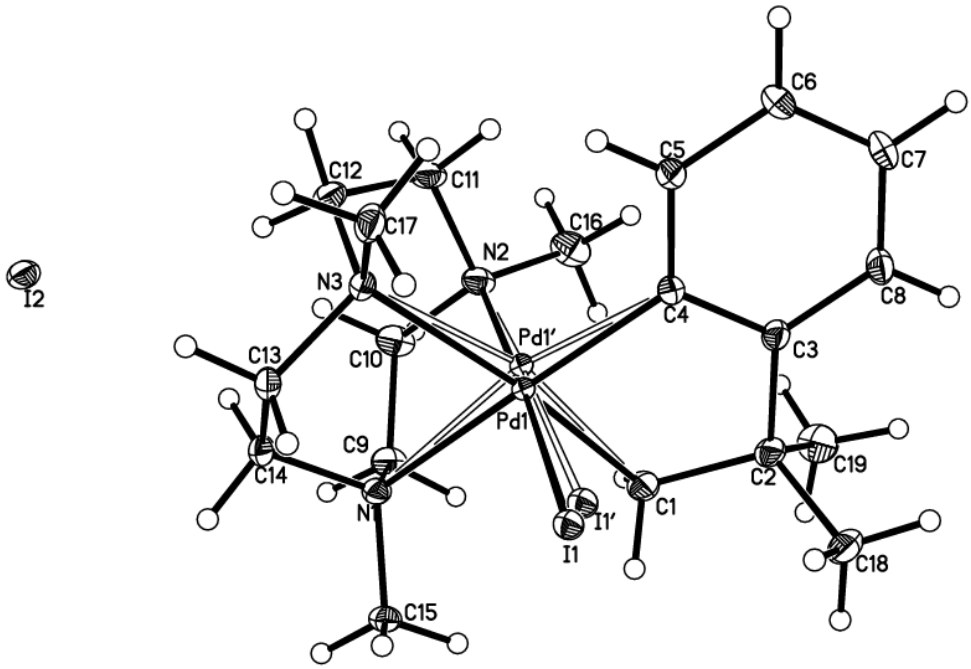
C(4)-Pd(1)-C(1)	81.42(6)
C(4)-Pd(1)-N(2)	92.52(6)
C(1)-Pd(1)-N(2)	96.60(6)
C(4)-Pd(1)-N(1)	171.17(6)
C(1)-Pd(1)-N(1)	92.91(6)
N(2)-Pd(1)-N(1)	81.36(5)
C(4)-Pd(1)-N(3)	105.56(6)
C(1)-Pd(1)-N(3)	172.63(6)
N(2)-Pd(1)-N(3)	80.94(6)
N(1)-Pd(1)-N(3)	79.88(5)
C(4)-Pd(1)-I(1)	88.66(4)
C(1)-Pd(1)-I(1)	88.48(5)
N(2)-Pd(1)-I(1)	174.90(4)
N(1)-Pd(1)-I(1)	97.99(4)
N(3)-Pd(1)-I(1)	93.97(4)
C(4)-Pd(1')-N(2)	102.8(4)
C(4)-Pd(1')-C(1)	80.1(2)
N(2)-Pd(1')-C(1)	99.3(3)
C(4)-Pd(1')-N(3)	112.8(3)
N(2)-Pd(1')-N(3)	88.6(3)
C(1)-Pd(1')-N(3)	163.2(4)
C(4)-Pd(1')-N(1)	165.9(4)
N(2)-Pd(1')-N(1)	83.5(2)
C(1)-Pd(1')-N(1)	86.6(3)
N(3)-Pd(1')-N(1)	79.58(19)
C(4)-Pd(1')-I(1')	79.6(3)
N(2)-Pd(1')-I(1')	176.2(3)
C(1)-Pd(1')-I(1')	78.2(3)
N(3)-Pd(1')-I(1')	93.1(2)
N(1)-Pd(1')-I(1')	93.5(2)
C(15)-N(1)-C(9)	108.30(13)
C(15)-N(1)-C(14)	109.74(12)
C(9)-N(1)-C(14)	111.03(13)
C(15)-N(1)-Pd(1)	115.25(10)
C(9)-N(1)-Pd(1)	102.15(9)
C(14)-N(1)-Pd(1)	110.14(10)
C(15)-N(1)-Pd(1')	121.7(2)
C(9)-N(1)-Pd(1')	98.14(19)
C(14)-N(1)-Pd(1')	107.26(17)
C(16)-N(2)-C(11)	108.14(13)
C(16)-N(2)-C(10)	109.59(14)

C(11)-N(2)-C(10)	110.75(13)
C(16)-N(2)-Pd(1')	115.36(19)
C(11)-N(2)-Pd(1')	99.4(2)
C(10)-N(2)-Pd(1')	113.0(2)
C(16)-N(2)-Pd(1)	115.83(11)
C(11)-N(2)-Pd(1)	103.49(10)
C(10)-N(2)-Pd(1)	108.88(9)
C(8)-C(3)-C(4)	119.25(15)
C(8)-C(3)-C(2)	122.32(14)
C(4)-C(3)-C(2)	118.42(13)
C(17)-N(3)-C(13)	107.04(13)
C(17)-N(3)-C(12)	110.00(12)
C(13)-N(3)-C(12)	111.04(13)
C(17)-N(3)-Pd(1')	119.93(19)
C(13)-N(3)-Pd(1')	107.4(2)
C(12)-N(3)-Pd(1')	101.3(2)
C(17)-N(3)-Pd(1)	119.27(10)
C(13)-N(3)-Pd(1)	101.88(9)
C(12)-N(3)-Pd(1)	107.30(10)
C(5)-C(4)-C(3)	119.90(14)
C(5)-C(4)-Pd(1')	118.7(2)
C(3)-C(4)-Pd(1')	120.0(2)
C(5)-C(4)-Pd(1)	123.91(11)
C(3)-C(4)-Pd(1)	115.85(11)
N(3)-C(17)-H(17A)	109.5
N(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(4)-C(5)-C(6)	120.15(14)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(2)-C(1)-Pd(1)	115.08(11)
C(2)-C(1)-Pd(1')	112.4(2)
C(2)-C(1)-H(1A)	108.5
Pd(1)-C(1)-H(1A)	108.5
Pd(1')-C(1)-H(1A)	115.1
C(2)-C(1)-H(1B)	108.5
Pd(1)-C(1)-H(1B)	108.5
Pd(1')-C(1)-H(1B)	104.4
H(1A)-C(1)-H(1B)	107.5
N(1)-C(14)-C(13)	112.57(13)
N(1)-C(14)-H(14A)	109.1
C(13)-C(14)-H(14A)	109.1
N(1)-C(14)-H(14B)	109.1
C(13)-C(14)-H(14B)	109.1
H(14A)-C(14)-H(14B)	107.8
N(3)-C(13)-C(14)	112.70(14)
N(3)-C(13)-H(13A)	109.1
C(14)-C(13)-H(13A)	109.1
N(3)-C(13)-H(13B)	109.1
C(14)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.8
N(1)-C(15)-H(15A)	109.5
N(1)-C(15)-H(15B)	109.5

H(15A)-C(15)-H(15B)	109.5
N(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(3)-C(2)-C(1)	107.77(12)
C(3)-C(2)-C(19)	111.20(13)
C(1)-C(2)-C(19)	108.12(16)
C(3)-C(2)-C(18)	110.30(15)
C(1)-C(2)-C(18)	112.23(13)
C(19)-C(2)-C(18)	107.24(14)
N(2)-C(11)-C(12)	113.36(13)
N(2)-C(11)-H(11A)	108.9
C(12)-C(11)-H(11A)	108.9
N(2)-C(11)-H(11B)	108.9
C(12)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7
N(1)-C(9)-C(10)	111.89(14)
N(1)-C(9)-H(9A)	109.2
C(10)-C(9)-H(9A)	109.2
N(1)-C(9)-H(9B)	109.2
C(10)-C(9)-H(9B)	109.2
H(9A)-C(9)-H(9B)	107.9
C(7)-C(8)-C(3)	120.53(15)
C(7)-C(8)-H(8)	119.7
C(3)-C(8)-H(8)	119.7
C(2)-C(18)-H(18A)	109.5
C(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(7)-C(6)-C(5)	120.27(15)
C(7)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
N(3)-C(12)-C(11)	112.16(13)
N(3)-C(12)-H(12A)	109.2
C(11)-C(12)-H(12A)	109.2
N(3)-C(12)-H(12B)	109.2
C(11)-C(12)-H(12B)	109.2
H(12A)-C(12)-H(12B)	107.9
N(2)-C(10)-C(9)	112.54(13)
N(2)-C(10)-H(10A)	109.1
C(9)-C(10)-H(10A)	109.1
N(2)-C(10)-H(10B)	109.1
C(9)-C(10)-H(10B)	109.1
H(10A)-C(10)-H(10B)	107.8
C(6)-C(7)-C(8)	119.88(15)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(2)-C(19)-H(19A)	109.5
C(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(2)-C(16)-H(16A)	109.5

N(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
N(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Projection view with 50% probability ellipsoids:



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