Supporting Information

Divergent Reactivity of Platinum(II) and Palladium(II) Methylperoxo Complexes and the Formation of an Unusual Hemi-Aminal Complex

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Experimental details

All moisture and dioxygen sensitive compounds were prepared using standard vacuum line, Schlenk or cannula techniques. A standard nitrogen filled glove box was used for any subsequent manipulation and storage of these compounds. NMR spectra were recorded using Bruker DRX-400 MHz, AV-400 MHz, AV-500 MHz spectrometers. The $^1$H NMR and $^{13}$C NMR chemical shifts were referenced to the residual protio impurity and $^{13}$C signal of the deuterated solvent, respectively. The $^{19}$F NMR chemical shifts were referenced to CFCl$_3$. Mass spectra were recorded using either a Micromass AutoSpec Premier spectrometer or a Waters LCT Premier spectrometer. Photolysis experiments were carried out in normal NMR tubes, either by exposure to bright sunlight or with the use of a UV lamp (365 nm, 100 W).

Solvents and Reagents

Diethyl ether and THF were dried by prolonged reflux, under a nitrogen atmosphere, over sodium metal with a benzophenone ketyl indicator and distilled freshly prior to use. DCM and acetonitrile were treated in a similar manner, but using calcium hydride as the drying agent. Toluene and pentane were dried by passing through a column, packed with commercially available Q-5 reagent (13 % CuO on alumina) and activated alumina.
(pellets, 3 mm), in a stream of nitrogen. Acetone was dried over B$_2$O$_3$ and distilled under nitrogen. All solvents were thoroughly deoxygenated before use. The following compounds were prepared according to literature procedures: 6,6”-diamino-2,2’:6’,2”-terpyridine, $^2$[Pt(OOCH)$_3$]SbF$_6$,$^2$ and [Pd(OOCH)$_3$]SbF$_6$.$^3$ All other chemicals were obtained commercially and used as received.

Preparation of [Pd{OC(CD$_3$)$_2$(1-H)}]SbF$_6$: A sample of [PdCH$_3$](SbF$_6$) (20 mg) in d$_6$-acetone (0.5 mL) was prepared in a glove box. Dioxygen was bubbled through the sample for 1 minute in the absence of light. The sample was exposed to sunlight (or UV light 365 nm, 100 W) and the reaction was monitored by $^1$H NMR spectroscopy. Consumption of the starting complex to give the methylperoxo complex [Pd(OOCH)$_3$](SbF$_6$) was complete typically within 5 minutes at room temperature. The final product [Pd{OC(CD$_3$)$_2$(1-H)}]SbF$_6$ was formed quantitatively. $^1$H NMR (500 MHz, d$_6$-acetone) δ 8.71 (br, 1H, NH$_{ext}$) 8.34 (t, 1H, J = 8 Hz, H4’), 8.23 (d, 1H, J = 8 Hz, H3’), 8.12 (d, 1H, J = 8 Hz, H4”), 7.76 (dd, 1H, J = 8, 8 Hz, H4), 7.73 (dd, 1H, J = 8, 8 Hz, H4”), 7.54 (dd, J = 7, 1 Hz, 1H, H3), 7.47 (dd, J = 7, 1 Hz, 1H, H3”), 7.27 (s, 1H, OC(CD$_3$)$_2$NH), 6.86 (dd, J = 2, 1 Hz, 1H, H5), 6.84 (dd, J = 2, 1 Hz, 1H, H5”), 6.65 (br, 1H, NH$_{int}$). $^{13}$C{$^1$H} NMR (125 MHz, d$_6$-acetone) δ 163.9, 155.8, 155.6, 155.3, 155.2, 154.8, 141.4 (C4’), 140.6, 140.3 (C4 + C4”), 123.3, 123.2 (C3’ + C5’), 118.4, 117.0 (C5 + C5”), 113.8, 112.9 (C3 + C3”), 84.7 (OC(NH)(CD$_3$)$_2$). The signal for OC(NH)(CD$_3$)$_2$ (septet) was too weak to be observed and may overlap with the solvent signal at 30 ppm. MS (+LSIMS, m/z (%)): 432 (60) [(M-SbF$_6$)$^+$], 369 (60) [(M-OC(CD$_3$)$_2$-SbF$_6$)$^+$].

Yellow crystals suitable for X-ray diffraction were obtained from an acetone solution of complex [Pd{OC(CH$_3$)$_2$(1-H)}]SbF$_6$, layered with hexane.

Crystal data for [Pd{OC(CH$_3$)$_2$(1-H)}]SbF$_6$: [C$_{18}$H$_{18}$N$_5$OPd](SbF$_6$), $M = 662.52$, monoclinic, $P2_1/n$ (no. 14), $a = 12.8162(3)$, $b = 8.13176(16)$, $c = 20.6429(5)$ Å, $\beta = 100.132(2)^\circ$, $V = 2117.82(8)$ Å$^3$, $Z = 4$, $D_c = 2.078$ g cm$^{-3}$, $\mu$(Mo-Kα) = 2.198 mm$^{-1}$, $T = 173$ K, yellow platy needles, Oxford Diffraction Xcalibur 3 diffractometer; 7140 independent measured reflections ($R_{int} = 0.0236$), $F^2$ refinement,$^4$ $R_1$(obs) = 0.0298,
$wR_2(\text{all}) = 0.0693$, 5857 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{\text{max}} = 65^\circ$], 335 parameters. CCDC 987857.
Figure S1. $^1$H NMR spectra of the starting complex [Pd(CH$_3$)(I)](SbF$_6$) (top) and the reaction with O$_2$ and sunlight in CD$_3$CN at 298 K to give [Pd(OOCH$_3$)(I)](SbF$_6$) (bottom).
Figure S2. $^1$H NMR spectrum (500 MHz, 298 K) of complex [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$) in d$_6$-acetone (s) (* = H$_2$O and HDO).
Figure S3. $^1$H NMR spectrum (500 MHz, 298 K) of complex [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$) in d$_6$-acetone.

The signals at 5.04 and 10.87 ppm show no interaction with any N or C atoms of the complex in the HSQC spectra, but they do interact with the H$_2$O signal at 2.6 ppm, as seen in the NOESY spectrum and are due to OH signals from free and coordinated CH$_3$OOH, respectively. The two singlets at 3.75 and 3.78 show no correlation with any of the other protons in the COSY and NOESY spectra. The $^1$H-$^{13}$C HSQC spectrum shows that the singlet at 3.75 ppm correlates with the signal at 64.7 ppm and the singlet at 3.78 ppm correlates to the signal at 63.7 ppm and, combined with the DEPT 135 results, these signals are assigned to CH$_3$ groups from CH$_3$OOH.
Figure S4. Expansion of the aromatic region of the $^1$H NMR spectrum (500 MHz, 298 K) of complex $[\text{Pd}\{\text{OC(CD}_3\}_2(1-\text{H})\}](\text{SbF}_6)$ in d$_6$-acetone.
Figure S5: COSY spectrum at 400 MHz, 298 K of [Pd\{OC(CD_3)_2(1-H)}\]_2(SbF_6) in d_6-acetone.
Figure S6. The aromatic region of the COSY spectrum at 400 MHz, 298 K of \([\text{Pd}\{\text{OC(\text{CD}_3)}_2(1-\text{H})}\}](\text{SbF}_6)\) in \(d_6\)-acetone.
Figure S7: NOESY spectrum at 500 MHz, 298 K of [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$) in d$_6$-acetone.
Figure S8: The aromatic region of the NOESY spectrum at 500 MHz, 298 K of [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$) in d$_6$-acetone.
Figure S9: $^1$H-$^{15}$N HSQC NMR spectrum at 500 MHz, 298 K of [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$) in d$_6$-acetone. The NH$_2$ signals are too broad to observed any correlation.
Figure S10: $^{13}$C$\{^1$H$\}$ NMR spectrum at 125 MHz, 298 K of [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$) in d$_6$-acetone.
Figure S11: $^1$H-$^{13}$C HSQC NMR spectrum at 500 MHz, 298 K of [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$) in d$_6$-acetone (s). (* = H$_2$O and HDO).
Figure S12: DEPT135 NMR spectrum at 125 MHz, 298 K of [Pd\{OC(CD_3)_2(1-H)}\}(SbF_6)] in d_6-acetone.
Figure S13. LSIMS positive ion mass spectrum of [Pd{OC(CD$_3$)$_2$(1-H)}](SbF$_6$). m/z = 432: [Pd{OC(CD$_3$)$_2$(1-H)}]$^+$; m/z = 368: [Pd(1-H)]$^+$. 

mol. ion for C18H12D6N5OPd
**The X-ray crystal structure of [Pd{OC(CH₃)₂(1-H)}₆](SbF₆)**

The NH and NH₂ hydrogen atoms in the structure of [Pd{OC(CH₃)₂(1-H)}₆](SbF₆) were located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å. The SbF₆ anion was found to be disordered. Two orientations were identified of ca. 91 and 9% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and the antimony atoms of both orientations and the fluorine atoms of the major occupancy orientation were refined anisotropically (the fluorine atoms of the minor occupancy orientation were refined isotropically).

**Figures**

![Structure of the cation](image)

**Fig. S14** The structure of the cation present in the crystal of [Pd{OC(CH₃)₂(1-H)}₆](SbF₆) (50% probability ellipsoids).

The cations in the structure of [Pd{OC(CH₃)₂(1-H)}₆](SbF₆) pack in a head-to-tail fashion via π-π interactions across two independent centres of symmetry to form an
extended stack of cations along the crystallographic $b$ axis direction (Figure S15). The N(19)-based pyridine ring in one cation links to the N(1) ring in a $C_i$-related counterpart (centroid···centroid and mean interplanar separations of ca. 3.71 and 3.37 Å, rings inclined by ca. 2°, interaction a in Figure S15), and also to the N(8) ring in another cation across the other centre of symmetry (centroid···centroid and mean interplanar separations of ca. 3.62 and 3.33 Å, rings inclined by ca. 3°, interaction b).

**Table S1.** Selected bond lengths (Å) and angles (°) for the cation present in the crystal of $\text{[Pd\{OC(CH₃)₂(1-H)\}]\text{(SbF}_₆\text{)}}$.  

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
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<td>1.928(2)</td>
<td>Pd–O(15)</td>
<td>1.9841(17)</td>
<td>Pd–N(8)</td>
<td>1.990(2)</td>
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<td>82.17(9)</td>
<td>N(8)–Pd–O(15)</td>
<td>94.67(8)</td>
<td>N(1)–Pd–O(15)</td>
<td>176.32(8)</td>
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<td>80.81(8)</td>
<td>O(15)–Pd–N(19)</td>
<td>102.41(7)</td>
<td>N(8)–Pd–N(19)</td>
<td>162.84(8)</td>
</tr>
</tbody>
</table>
Figure S15. Part of one of the π-π linked stacks of cations along the b axis direction present in the crystal of [Pd{OC(CH₃)₂(1-H)}](SbF₆). The π-π stacking interactions have centroid···centroid and mean interplanar separations (Å) of a) 3.71, 3.37, and b) 3.62, 3.33 respectively.

References

(4)  (a) SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-97, G.M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122; (c) SHELX-2013, http://shelx.uni-ac.gwdg.de/SHELX/index.php.