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One-Electron Oxidation of [M(P^tBu_3)_2] (M = Pd, Pt): Isolation of Monomeric [Pd(P^tBu_3)_2]^+ and Redox-Promoted C–H Bond Cyclometalation

Thibault Troadec, Sze-yin Tan, Christopher J. Wedge, Jonathan P. Rourke, Patrick R. Unwin, and Adrian B. Chaplin*

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1 Synthesis of new compounds

1.1 General methods

All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques. Glassware was oven dried at 150°C overnight and flamed under vacuum prior to use. Anhydrous CH2Cl2, THF and pentane (<0.005% H2O) were purchased from ACROS or Sigma-Aldrich and freeze-pump-thaw degassed three times before being placed under argon. CD2Cl2 was dried over CaH2, vacuum distilled, and freeze-pump-thaw degassed three times before being placed under argon. 1,2-Difluorobenzene (DiFB) was stirred over neutral aluminum oxide, filtered, dried over CaH2, vacuum distilled, and freeze-pump-thaw degassed three times before being placed under argon over 3 Å molecular sieves. [Pd(PtBu3)2] (1a), [Pt(PtBu3)2] (1b) and [Fc][PF6] were purchased from Sigma-Aldrich and used as received. Na[BArF4] was synthesised using a literature protocol. 1

[Fc][BArF4] was prepared using an adapted literature procedure. 2 A suspension of [Fc][PF6] (120 mg, 0.362 mmol) and Na[BArF4] (354 mg, 0.398 mmol) in dry CH2Cl2 (15 mL) was stirred at room temperature for 3 h. The solution was filtered and layered with pentane to afford deep blue needles that were subsequently isolated by filtration and washed with pentane (2 × 10 mL). Yield = 278 mg (75%). 19F{1H} NMR (282 MHz, CD2Cl2): δ -63.6 (s, ArF).

All other solvents and reagents are commercial products and were used as received.

NMR spectra were recorded on Bruker DPX-400, AV-400, AV-500, AVIIIHD-500 and AVIII-600 spectrometers at 298 K unless otherwise stated. 1H NMR spectra recorded in DiFB were referenced using the highest intensity peak of the highest (δ 6.87) frequency fluoroarene multiplet. An internal sealed capillary of 0.25 M OP(OMe)3 in C6D6 was used to lock and shim samples for acquisition of NMR data, and additionally act as an internal reference for 1H and 31P{1H} NMR data. Chemical shifts are quoted in ppm and coupling constants in Hz. EPR spectra were acquired on a Bruker EMX spectrometer using a TM130 cylindrical mode resonator (ER 4103TM). Samples were cooled by nitrogen gas flow through a standard quartz insert from a nitrogen evaporator with a B-VT 2000 temperature control unit. To limit the dielectric loss arising from the solvent all samples were contained in 2.2 mm i.d. quartz tubes (Wilmad 705-SQ), and the quartz insert was removed for room temperature operation. The reported g-factor is referenced to a DPPH standard (g = 2.0036(3), ref. 3) and all EPR spectra are background subtracted unless otherwise noted. The background was recorded for a sample of [Fc][BArF4] in DiFB under identical conditions giving a featureless spectrum attributed to cavity background (see Figure S18).

ESI-HRMS analyses were recorded on Bruker Maxis Impact instrument.

Microanalyses were performed by Stephen Boyer at London Metropolitan University.
1.2 Preparation of [Pd(P^3Bu_3)_2][PF_6] (2a)

A suspension of [Pd(P^3Bu_3)_2] (1a, 40 mg, 0.078 mmol) and [Fc][PF_6] (24 mg, 0.078 mmol) in DiFB (3 mL) was stirred at room temperature for 2 h. The solution was filtered and the product precipitated with pentane as a Persian blue solid. Yield = 47 mg (92%).

**EPR** (15 mM in DiFB, 200 K): $g_{iso} = 2.316(5)$, $a(^{105}\text{Pd}) = 25 \text{ mT}$.

**ESI-HRMS** (THF, 180 °C, 3 kV): positive ion: 510.2736 m/z, [M]+ (calcd. 510.2740 m/z).

**UV-Vis**: (0.15 mM in DiFB, 293 K): $\lambda_{max}$ ($\varepsilon$) 667 nm (4500 ± 200 M$^{-1}$·cm$^{-1}$). First order decrease of this peak is observed at 293 K ($k_{obs} = 0.00039$ min$^{-1}$). When ca. 100 equiv. of water was added an increased rate of decomposition was measured ($k_{obs} = 0.00076$ min$^{-1}$).

**Anal.** Calcd for C$_{24}$H$_{54}$F$_6$P$_3$Pd (656.03 g·mol$^{-1}$): C, 43.94; H, 8.30; N, 0.00. Found: C, 44.03; H, 8.17; N, 0.00.

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![Figure S1](image1.png)

Figure S1. ESI-HRMS of 2a: observed (above) and calculated (below).

![Figure S2](image2.png)

Figure S2. UV-Vis spectrum of 2a in 1,2-C$_6$H$_4$F$_2$ (293 K).
1.3 Preparation of 2,6-bis(decyl)pyridine

To a cooled and stirred solution of lutidine (2.0 mL, 17.3 mmol) in dry THF (60 mL, -78°C) was added \(^{6}BuLi\) (1.6 M in hexanes, 25.6 mL, 41.0 mmol) dropwise. Upon addition, the colourless solution turned bright orange and then red. After 30 minutes stirring at -78°C, 1-bromononane (7.47 mL, 39 mmol) was added and solution slowly warmed to room temperature over 16 h. The mixture was carefully quenched with water (10 mL) and the organic phase extracted with hexane (3 x 40 mL), washed with water (3 x 10 mL) and dried over MgSO\(_4\). Volatiles were removed under vacuum and the residue was purified by silica column chromatography (hexane/ethyl acetate 20:1) to afford the product as a colourless liquid. Yield = 4.10 g (66%).

\(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 (t, \(J_{HH} = 7.7, 1H, Py\)), 6.93 (d, \(J_{HH} = 7.7, 2H, Py\)), 2.74 (app t, \(J = 7.9, 4H, Py-CH\(_2\))

1.4 Preparation of [Pt(\(k^2_{PC}-P^{Bu}_{2}CMe_{2}CH_{2})(P^{Bu}_{2})][PF_{6}]\) (3b)

A solution of [Pt(\(P^{Bu}_{2})\)] (1b, 75 mg, 0.13 mmol) in DiFB (2 mL) was added dropwise to a mixture of [Fc][PF\(_6\)] (87 mg, 0.26 mmol) and 2,6-bis(decyl)pyridine (225 mg, 0.63 mmol) in DiFB (2 mL). After 12 h stirring, the solution was filtered, the volatiles were removed under vacuum, and the residue was washed with pentane. The crude product was recrystallised from DiFB/pentane to afford the product as yellow crystals. Yield = 86 mg (93%).

\(^{1}H\) NMR (600 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 2.75 (br d', \(J_{PH} = 7.8, J_{PH} = 110, 2H, PtCH\(_2\))

\(^{19}C\) NMR (126 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 56.9 (br d, \(J_{PC} = 19, P^{Bu}_{2}CMe_{2}CH_{2}\)), 42.1 (dd, \(J_{PC} = 14, J_{PC} = 2, P^{Bu}_{2}[C]\)), 32.4 (\(P^{Bu}_{2}CMe_{2}CH_{2}[CH_{3}]\)), 32.1 (\(P^{Bu}_{2}(CH_{2})\)), 30.5 (s', \(J_{PC} = 81, P^{Bu}_{2}CMe_{2}CH_{2}\)), 10.3 (br d', \(J_{PC} = 22, J_{PC} = 670, PtCH\(_2\))

\(^{1}P\) NMR (243 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 59.1 (d, \(J_{PP} = 317, J_{PP} = 2896, 1P, P^{Bu}_{2}\)), 25.2 (d, \(J_{PP} = 317, J_{PP} = 1916, 1P, P^{Bu}_{2}CMe_{2}CH_{2}\)), -144.8 (sept, \(J_{PP} = 710, 1P, PF_{6}\)).

\(^{195}Pt\) NMR (from \(^{1}H–^{195}Pt\) HMBC experiment, CD\(_2\)Cl\(_2\), 225 K): \(\delta\) -3816.

ESI-HRMS (CH\(_3\)CN, 180 °C, 3 kV): positive ion: 598.3284 m/z, [M+\(^{1}H\)]\(^{+}\) (calcd. 598.3265 m/z).

Anal. Calcd for C\(_{24}H_{53}F_{6}P_{3}Pt\) (743.68 g·mol\(^{-1}\)): C, 38.76; H, 7.18; N, 0.00. Found: C, 38.90; H, 7.33; N, 0.00.

ESI-4
Figure S3. $^1$H NMR spectrum of 3b (CD$_2$Cl$_2$, 600 MHz, 298 K) – inserts not to scale.

Figure S4. $^1$H NMR spectrum of 3b (CD$_2$Cl$_2$, 600 MHz, 185 K).

Figure S5. $^{31}$P{¹H} NMR spectrum of 3b (CD$_2$Cl$_2$, 243 MHz, 298 K).
Assignments from $^1$H–$^{15}$C HSQC and HMBC experiments.

$^{31}$Pt $^1$H NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ -19.9 (s', $^1$J$_{pp} = 3105$, 1P, P$^3$Bu$_2$CMe$_2$CH$_2$), -144.4 (sept, $^1$J$_{pp} = 710$, 1P, PF$_6$).

$^{195}$Pt NMR (from $^1$H–$^{195}$Pt HMOC experiment, CD$_2$Cl$_2$, 225 K): $\delta$ -3788.

ESI-HRMS (CH$_3$CN, 180 °C, 3 kV): positive ion: 552.2113 m/z, [M]$^+$ (calcd. 552.2104 m/z).

**Anal.** Calcd for C$_{24}$H$_{33}$P$_2$Pt (697.54 g/mol$^{-1}$): C, 37.88; H, 4.91; N, 4.02. Found: C, 37.96; H, 4.97; N, 3.87.
**Figure S7.** $^1$H NMR spectrum of 6 (CD$_2$Cl$_2$, 600 MHz, 298 K) – inserts not to scale.

**Figure S8.** $^{31}$P{$^1$H} NMR spectrum of 6 (CD$_2$Cl$_2$, 202 MHz, 298 K).

**Figure S9.** Most relevant section of the $^1$H–$^{195}$Pt HMQC spectrum of 6 (CD$_2$Cl$_2$, 225 K).
2 NMR scale reaction details

2.1 $^{31}$P Chemical shifts in 1,2-C$_6$H$_4$F$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{31}$P</th>
<th>Coupling constants / Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>P'tBu$_3$</td>
<td>62.2</td>
<td></td>
</tr>
<tr>
<td>[HP'tBu$_3$][PF$_6$]</td>
<td>ca. 55</td>
<td></td>
</tr>
<tr>
<td><a href="1a">Pd(P'tBu$_3$)$_2$</a></td>
<td>84.8</td>
<td></td>
</tr>
<tr>
<td><a href="1b">Pt(P'tBu$_3$)$_2$</a></td>
<td>100.1</td>
<td>$^1J_{pp} = 4408$</td>
</tr>
<tr>
<td>[Pt($k^2$pc-P'Bu$_2$CMe$_2$CH$_2$)(P'Bu$_3$)][PF$_6$] (3b)</td>
<td>24.3, 59.0</td>
<td>$^1J_{pp} = 1916, 2898$; $^2J_{pp} = 317$</td>
</tr>
<tr>
<td>[Pt(P'tBu$_3$)$_2$H][PF$_6$] (4)</td>
<td>86.3</td>
<td>$^1J_{pp} = 2621$</td>
</tr>
<tr>
<td>[Pt($k^2$pc-P'Bu$_2$CMe$_2$CH$_2$)(bipy)][PF$_6$] (6)</td>
<td>-20.1</td>
<td>$^1J_{pp} = 3105$</td>
</tr>
</tbody>
</table>

All relative to an internal sealed capillary containing OP(OMe)$_3$/C$_6$D$_6$

[$\delta^{31}$P 3.1, $\delta^{1}$H 3.36 ($^3J_{pp} = 11.0$)]

2.2 General conditions

Reactions were carried in 5 mm J. Young’s valve NMR tubes using 0.015 mmol complex (i.e. 7.7 mg 1a, 9.0 mg 1b, 9.9 mg 2a, 11.2 mg 3b) in DiFB (0.50 mL) solvent and an internal capillary containing 60 μL of a 0.25 M solution of trimethylphosphate in C$_6$D$_6$. Reactions were monitored by $^1$H and $^{31}$P NMR spectroscopy.

2.3 Reactions of [Pd(P'tBu$_3$)$_2$] (1a)

2.3.1 1a @ 293 K

No change apparent after 24 h.

2.3.2 1a + 1 equiv. [Fc][PF$_6$] @ 293 K

No diamagnetic species observed in the $^{31}$P($^1$H) NMR spectrum after 15 min. The $^1$H NMR spectrum showed the presence of Fc ($\delta^{1}$H 4.14).

2.3.3 1a + 5 equiv. 2,6-bis(decyl)pyridine @ 293 K

No reaction apparent after 24 h.

2.3.4 1a + 2 equiv. [Fc][PF$_6$] + 5 equiv. 2,6-bis(decyl)pyridine @ 293 K

Slow formation of a new organometallic species characterised by two doublets in the $^{31}$P($^1$H) NMR spectrum in a 1:1 ratio ($\delta^{31}$P 57.0, -1.3; $^2J_{pp} = 316$ Hz). After 72 h an approximate conversion of 30% was determined using the internal reference (Figure S10).
2.4 Reactions of [Pt(P^tBu_3)_2] (1b)

2.4.1 1b @ 293 K

No change apparent after 24 h.

2.4.2 1b @ 353 K

No change apparent after 24 h.

2.4.3 1b + 1 equiv. [Fc][PF_6] @ 293 K

1:1 mixture of 3b and 4 formed within 15 min by ^31P NMR spectroscopy. Integration against the internal standard indicates complete conversion. The ^1H NMR spectrum showed the presence of Fc (δ_{^1H} 4.01).

2.4.4 1b + 5 equiv. 2,6-bis(decyl)pyridine @ 293 K

No reaction apparent after 24 h.

2.4.5 1b + 2 equiv. [Fc][PF_6] + 5 equiv. 2,6-bis(decyl)pyridine @ 293 K

Integration against the internal standard indicated complete conversion to 3b within 15 min. The ^1H NMR spectrum showed the presence of Fc (δ_{^1H} 4.63).

2.4.6 1b + 1 equiv. [Fc][PF_6] + 1 equiv. 2,2'-bipyridine @ 293 K

Integration against the internal standard indicated formation of a mixture comprised of 1b, 6, P^tBu_3 and [HP^tBu_3]^+ (~1:1:0.3:0.7) by ^31P NMR spectroscopy after 15 min. The ^1H NMR spectrum showed the presence of Fc (δ_{^1H} 3.97).

2.4.7 1b + 2 equiv. [Fc][PF_6] + 1 equiv. 2,2'-bipyridine @ 293 K

Integration against the internal standard indicated complete conversion to a ~1:1 mixture comprised of 6 and [HP^tBu_3]^+ by ^31P NMR spectroscopy after 15 min. The ^1H NMR spectrum showed the presence of Fc (δ_{^1H} 3.97).
2.5 Reactions of [Pd(P^3Bu_3)_2][PF_6] (2a)

2.5.1 2a @ 293 K

No new diamagnetic species observed in either the ^1H or ^31P(^1H) NMR spectrum after 24 h.

2.6 Reactions of [Pt(κ^2_Pc-P^3Bu_2CMe_2CH_2)(P^3Bu_3)][PF_6] (3b)

2.6.1 3b @ 293 K

No change apparent after 24 h.

2.6.2 3b + H_2 (1 atm) @ 293 K

Complete conversion to 4 after 1 h shaking apparent by ^1H and ^31P NMR spectroscopy. After freeze-pump-thaw-degassing and placing under an argon atmosphere, no additional reaction was apparent after 15 min (δ_H = -36.30, J_HH = 8.6, J_PtH = 2590 Hz; δ_P = 86.3, J_PtP = 2621 Hz; Figure S11 and S12).

![Figure S11](image1.png)

**Figure S11.** ^1H NMR spectrum of 4 (DiFB, 500 MHz, 298 K).

![Figure S12](image2.png)

**Figure S12.** ^31P(^1H) NMR spectrum of 4 (DiFB, 202 MHz, 298 K).

To the mixture described above was added 5 equiv. of 2,6-bis(decyl)pyridine, resulting in deprotonation of 4 and formation of an equilibrium mixture of 1b and 4 in a 1:7 ratio (by ^31P NMR).
spectroscopy) after 15 min (ratio unchanged after an additional 45 min).

2.6.3 3b + 1 equiv. 2,2'-bipyridine @ 293 K
Quantitative formation of 6 with concomitant liberation of free P^tBu_3 was observed within 15 min by $^{31}$P NMR spectroscopy.

3 Electrochemistry

3.1 General methods
Cyclic voltammetry (CV) experiments were carried out in an inert atmosphere glovebox under argon out using a CHI 760 C potentiostat (CH Instruments, Inc.) in a typical 3-electrode set-up where a glassy carbon substrate, platinum mesh and silver wire were used as the working (WE), counter (CE) and reference electrode (RE), respectively. All potentials are calibrated to the ferrocene/ferrocenium (Fc/[Fc]^+) redox couple which was used as an internal standard.

The half-wave potentials, $E_{1/2}$, were determined from:

$$E_{1/2} = \frac{E_{p^{\text{ox}}} + E_{p^{\text{red}}}}{2}$$

where $E_{p^{\text{red}}}$ and $E_{p^{\text{ox}}}$ are the reduction and oxidation peak potentials, respectively.

3.2 Fc/[Fc]^+ redox couple in 1,2-C_6H_4F_2 / 0.2 M [^tBu_4N][PF_6]
Figure S13 shows typical CVs for the oxidation of Fc at different scan rates. Linear dependence of the voltammogram peak current, $i_p$, to square root of the potential sweep scan rate, $\nu^{1/2}$ indicates a diffusion-controlled process.

![Figure S13](image)

**Figure S13.** (a) CVs for the oxidation of Fc in 1,2-C_6H_4F_2 (2 mM; 0.2 M[^tBu_4N][PF_6]) electrolyte; scan rates = 10, 30, 50, 70 and 100 mV s^{-1}); (b) Plot of $i_p$ and $\Delta E_p$ versus $\nu^{1/2}$. 

ESI-11
The peak-to-peak potential separation, \( \Delta E_p \), is 108 mV at \( v = 100 \text{ mV s}^{-1} \) which deviates from the expected value of 60 mV (reversible) for the Fc/[Fc]** redox couple.\(^4\) This is reasonably attributed to the high internal resistance of the solution arising from incomplete ionic dissociation resulting in ohmic resistance of \( \sim 1 \text{ K}\Omega \). Furthermore, \( i_p^{\text{red}} / i_p^{\text{ox}} \sim 0.99 \) is characteristic of a chemically reversible process.

### 3.3 Reduction of isolated 2a

![CVs for the oxidation of 1a and reduction of 2a](image)

**Figure S14.** CVs for the oxidation of 1a and reduction of 2a in 1,2-C\(_6\)H\(_4\)F\(_2\) (2 mM [Pd]; 0.2 M \([n\text{Bu}_4\text{N}][\text{PF}_6]\) electrolyte; scan rates = 10, 30, 50, 70 and 100 mV s\(^{-1}\)).

### 3.4 Reduction of isolated 3b\(^5\) and 6

![CVs for the reduction of 3b and 6](image)

**Figure S15.** CVs for the reduction of 3b and 6 in 1,2-C\(_6\)H\(_4\)F\(_2\) (2 mM [Pt]**; 0.2 M \([n\text{Bu}_4\text{N}][\text{PF}_6]\) electrolyte; glassy carbon working electrode, Pt counter electrode and Ag wire reference electrode; scan rates = 10, 30, 50, 70 and 100 mV s\(^{-1}\)).

### 3.5 Additional details

Diffusion coefficients, \( D \), were determined using the Randle-Sevcik\(^4\) equation:

\[
i_p = 2.69 \times 10^5 \, n^{3/2} \, ACD^{1/2} \, v^{1/2}
\]

where \( n \) is the number of electrons transferred per redox event, \( A \) is the electrode area and \( C \) is the concentration.
Table S1. Calculated diffusion coefficients from Randle-Sevcik analysis (1,2-C₆H₄F₂, 0.2 M [³Bu₄N][PF₆] electrolyte)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R^2$ (fit)</th>
<th>$D / 10^{-6}$ cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc</td>
<td>0.99995</td>
<td>7.6</td>
</tr>
<tr>
<td>1a</td>
<td>0.99964</td>
<td>6.9</td>
</tr>
<tr>
<td>1b</td>
<td>0.99938</td>
<td>5.3</td>
</tr>
<tr>
<td>2a</td>
<td>0.99836</td>
<td>5.9</td>
</tr>
<tr>
<td>3b</td>
<td>0.99780</td>
<td>7.6</td>
</tr>
<tr>
<td>6</td>
<td>0.99950</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Figure S16. Plots of $i_p$ versus $\nu^{1/2}$ for 1a, 1b, 2a, 3b and 6.
4 EPR Spectroscopy

![EPR Spectra](image)

Figure S17. EPR spectra of 2a and [Fc][BAR\textsubscript{2}F\textsubscript{4}] (1,2-C\textsubscript{6}H\textsubscript{4}F\textsubscript{2} glass, 200 K, a.u. = arbitrary units) without baseline correction.

5 Crystallography

Full crystallographic details including solution, refinement and disorder modelling procedures are documented in CIF format and have been deposited with the Cambridge Crystallographic Data Centre under CCDC 1440602 (2a), 1440603 (3b) 1440604 (6, C\textsubscript{2}e/c) and 1440605 (6, P2\textsubscript{1}1/c). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Notably two different solid-state structures for 6 were obtained. Both sets of data were collected from crystals grown from the same solvent, but the samples crystallised in different space groups. In the P2\textsubscript{1}1/c structure the cation and anion are extensively disordered over two sites (Figure S18, left), however, only a small degree of disorder is observed in the C\textsubscript{2}e/c structure (Figure S18, right). In the latter case, only disorder of the (heavy) platinum atom was modelled due to the very low occupancy of the minor component (5%).

The data presented in Figure 3 is from the C\textsubscript{2}e/c structure.

![Solid-state structures](image)

Figure S18. Solid-state structures of 6: P2\textsubscript{1}1/c (left, CCDC 1440605) and C\textsubscript{2}e/c (right, CCDC 1440604). Thermal ellipsoids drawn at 50% probability level. Minor disordered components labelled in grey and bearing A as a suffix. Selected data: P2\textsubscript{1}1/c, Pt1–Pt1A, 1.050(2) Å; C\textsubscript{2}e/c, Pt1–Pt1A, 0.995(7) Å.
6 References and notes


[5] No oxidation of 3b is observed on scanning the potential up to +1.0 V vs Fc/[Fc]^+.