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#### **Supporting Information**

## **Platinum corroles**

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#### **Experimental section**

**Materials.** Free-base *meso*-triarylcorroles were synthesized according to a literature procedure.<sup>1</sup> *p*-Methylphenylmagnesium bromide (0.5 M in diethyl ether) and anhydrous benzonitrile were purchased from Sigma-Aldrich and used as received. Platinum(II) chloride was purchased from Sigma-Aldrich and used to synthesize tetranuclear platinum(II) acetate, as described in the literature.<sup>2</sup> Platinum insertion reactions were carried out in a Biotage Microwave reactor using 10-20 mL microwave vials. Silica gel 60 (0.04-0.063 mm particle size, 230-400 mesh, Merck) and activated, neutral alumina (Brockmann I, Sigma-Aldrich) were employed for flash chromatography. Silica gel 60 preparative thin-layer chromatographic plates (20 x 20 cm; 0.5 mm thick, Merck) were used for final purification of all complexes.

**Instrumental methods**. UV-visible spectra were recorded on an HP 8453 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a 400-MHz Mercury Plus Varian spectrometer at room temperature in CDCl<sub>3</sub> and referenced to residual CHCl<sub>3</sub> 7.26 ppm. MALDI-TOF (α-cyano-4-hydroxycinnamic acid used as matrix) and LDI mass spectra were recorded on a Waters Micromass MALDI micro MX Mass Spectrometer. Highresolution ESI mass spectra were recorded on a Thermo Sceintific LTQ Orbitrap XL<sup>TM</sup> spectrometer in positive mode using methanol as a carrier solvent.

Cyclic voltammetry was carried out at 298 K with an EG&G Model 263A potentiostat having a three electrode system: a glassy carbon working electrode, a platinum wire counterelectrode, and a saturated calomel reference electrode (SCE). Tetra(*n*butyl)ammonium perchlorate, recrystallized twice from absolute ethanol and dried in a desiccator for at least 2 weeks, was used as the supporting electrolyte. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (Aldrich) was used as solvent. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The electrolyte solution was purged with argon for at least 2 min and all measurements were carried out under an argon blanket. All potentials were referenced to the SCE.

<sup>&</sup>lt;sup>1</sup> Koszarna, B.; Gryko, D. T. J. Org. Chem. 2006, 71, 3707-3717.

<sup>&</sup>lt;sup>2</sup> Basato, M.; Biffis, A.; Martinati, G.; Tubaro, C.; Venzo, A.; Ganis, P.; Benetollo, F. *Inorg. Chim. Acta* 2003, **355**, 399-403.

EPR spectra were recorded on a Bruker ELEXSYS E500 spectrometer equipped with a SuperX CWR bridge, an ER 4116DM dual mode cavity, an ER 4112HV cryostat, an Oxford Instruments ITC 503 temperature controller, an EIP 538B frequency counter and an ER035M NMR Gauss-meter. Spectra were recorded on ground solid samples, in 2:1 dichloromethane/toluene at room temperature, and on frozen glasses obtained from the same solutions at 73 K. The spectra were simulated using home-written software.<sup>3</sup>

Preliminary experiments aimed at Pt insertion. Insertion of Pt into corroles proved to be an extraordinarily unpredictable endeavor. The choice of the platinum precursor, the solvent, and other details of reaction conditions (temperature and aerobic/anerobic conditions) each proved to be critically important to Pt insertion and the isolation of Pt corrole products. Platinum insertion failed to occur in toluene, pyridine, dichloromethane, chloroform, THF, methanol, ethanol, acetic acid, DMF, and DMSO, before finally taking place in benzonitrile. In the same vein, all commercially available platinum precursors, including PtCl<sub>2</sub>, Pt(acac)<sub>2</sub>, transplatin, PtCl<sub>4</sub>, and K<sub>2</sub>PtCl<sub>6</sub> failed to lead to Pt insertion. Use of Pt(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, which we synthesized via a literature procedure,<sup>2</sup> in pyridine led to Pt insertion into a number of different *meso*-triarylcorroles, evidenced in each case by a [Pt(corrole)]<sup>+</sup> molecular ion in a MALDI-TOF mass spectrum, but the complexity of the product mixtures and difficulties with isolation forced us to abandon this approach. Encouraged by this preliminary result, we continued our search and finally found the tetranuclear platinum acetate complex, [Pt(OAc)<sub>2</sub>]<sub>4</sub>•2HOAc, which is commercially unavailable and had to be synthesized by a literature method,<sup>2</sup> to be a suitable precursor. No Pt insertion could be detected up to 130 °C, but heating free-base corroles with platinum acetate in benzonitrile at 140 °C for 16 hours led to very low yields of diamagnetic Pt(IV) corrole products. Microwave irradiation of the same reaction mixture at 140-150 °C for 2 hours led to the same Pt(IV) corroles in a reproducible manner, albeit still in rather low ( $\sim 6\%$ ) yields.

<sup>&</sup>lt;sup>3</sup> Scheifele, Q.; Birk, T.; Bendix, J.; Tregenna-Piggott, P. L. W.; Weihe, H. Angew. Chem. Int. Ed. 2008, 47, 148-150.

General procedure for the synthesis of Pt{T(p-X-Ph)C}(o/m/p-

 $C_6H_4CN$ )(PhCN), where X = CF<sub>3</sub>, H, CH<sub>3</sub>, OCH<sub>3</sub>. To a 10-20 mL microwave vial charged with PhCN (10 mL) and a magnetic stirring bar were added the free-base corrole  $H_3[T(p-X-P)C]$  (0.054 mmol) and  $Pt_4(OAc)_8$ •2HOAc (1 equiv). The vial was sealed and heated for 2 h at 150 °C. After cooling, the contents of the vial were transferred to a roundbottom flask (100 mL) and evaporated to dryness. The crude product was dissolved in dichloromethane (5 mL) and loaded onto a silica gel column and eluted with a mixture of dichloromethane and *n*-hexane (the exact ratio being stated below for each case). All fractions containing Pt{T(p-X-Ph)C}(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN), with a  $\lambda_{max}$  between 426 and 430 nm, were collected and evaporated to dryness. A second column chromatography was carried out on a neutral alumina column, initially with pure dichloromethane to remove fast-eluting impurities, followed by a mixture of chloroform/dichloromethane. The Pt{T(p-X-Ph)C $(o/m/p-C_6H_4CN)$ (PhCN) product mixture thus obtained obtained was separated into the o, m, and p products via preparative thin-layer chromatography (PLC) with a dichloromethane/n-hexane mixture as eluent. In general, the quantities of the *ortho* isomers obtained were too meagre to permit full spectroscopic characterization. Additional details are provided below for individual compounds.

Synthesis and separation of Pt{T(p-CF<sub>3</sub>-Ph)C}(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). The crude reaction product was initially chromatographed on a silica gel column with 3:2 dichloromethane/n-hexane as eluent. Fractions containing different Pt{T(p-CF<sub>3</sub>-Ph)C}(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN) regioisomers, all with a  $\lambda_{max}$  of 430 nm, were collected and evaporated to dryness. A second column chromatography was then performed on a neutral alumina column, first with pure dichloromethane to remove the fast-eluting impurities, and then with 3:1 chloroform/dichloromethane, giving a combined yield of 3.69 mg (6.6 %) for the three isomers. PLC with 1:1 dichloromethane/n-hexane as eluent was then used to separate the isomers; the top band was identified as Pt{T(p-CF<sub>3</sub>-Ph)C}(m-C<sub>6</sub>H<sub>4</sub>CN)(PhCN), the middle one as the *para* isomer, and the lower one as the *ortho* isomer. Dark purple X-ray quality crystals of the *meta* isomer were grown by slow evaporation of a dichloromethane/n-hexane solution of the complex over a period of 15

days. Unfortunately, as discussed above, the structure was too strongly disordered to be

significantly useful. Detailed characterization of the *meta* and *para* isomers are as follows; the NMR assignments follow the abbreviations shown in Figure 2.

**Pt{T(***p***-CF<sub>3</sub>-Ph)C}(***m***-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). Yield 2.15 mg (3.52 %). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): \lambda\_{max} [nm, \varepsilon x 10<sup>-4</sup> (M<sup>-1</sup>cm<sup>-1</sup>)]: 430 (8.66), 502 (0.05), 532 (0.21), 571 (0.98), 595 (2.14). <sup>1</sup>H NMR: δ 9.16 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, \beta-H); 8.92 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, \beta-H ); 8.73 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, \beta-H); 8.67 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, \beta-H ); 8.43 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***o***1); 8.37 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***o***2); 8.25 (overlapping doublets, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 10-***o***1 and 10-***o***2); 8.07 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***m***1); 8.04 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***m***2); 8.00 (overlapping doublets, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 10-***m***1 and 10-***m***2); 6.33 [t, 1H,** *p* **(PhCN)]; 5.72 [d, 1H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz,** *p* **(C<sub>6</sub>H<sub>4</sub>CN)]; 5.48 [dd, 2H,** *m* **(PhCN)]; 5.00 [dd, 1H,** *m* **(C<sub>6</sub>H<sub>4</sub>CN)]; 1.75 [broad doublet, 2H,** *o* **(PhCN)], 0.57 [d, 1H,** *o***2 (C<sub>6</sub>H<sub>4</sub>CN) overlapping with s, 1H,** *o***1 (C<sub>6</sub>H<sub>4</sub>CN)]. MS (MALDI-TOF, major isotopomer): M<sup>+</sup> = 1126.85 (expt), 1126.19 (calcd for C<sub>54</sub>H<sub>29</sub>N<sub>6</sub>F<sub>9</sub>Pt).** 

Pt{T(*p*-CF<sub>3</sub>-Ph)C}(*p*-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). Yield 1.12 mg (1.83 %). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (nm), [ε x 10<sup>-4</sup> (M<sup>-1</sup>cm<sup>-1</sup>)]: 430 (6.72), 502 (0.06), 533 (0.44), 574 (0.78). <sup>1</sup>H NMR: δ 9.16 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz, β-H); 8.92 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz, β-H); 8.73 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz, β-H); 8.67 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz, β-H); 8.42 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*o*1-Ph); 8.35 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*o*2-Ph); 8.24 (overlapping doublets, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 10-*o*1-Ph & 10-*o*2-Ph); 8.06 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*m*1-Ph); 8.04 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*m*2-Ph); 8.00 (overlapping doublet, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 10-*m*1-Ph & 10-*m*2-Ph); 6.33 [t, 1H, *p* (PhCN)]; 5.46 [dd, 2H, *m* (PhCN)]; 5.19 [d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, *m* (C<sub>6</sub>H<sub>4</sub>CN)]; 1.70 [broad doublet, 2H, *o* (PhCN)], 0.46 [d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, *o* (C<sub>6</sub>H<sub>4</sub>CN)]. MS (MALDI-TOF, major isotopomer): M<sup>+</sup> = 1126.82 (expt), 1126.19 (calcd for C<sub>54</sub>H<sub>29</sub>N<sub>6</sub>F<sub>9</sub>Pt).

Synthesis and separation of Pt(TPC)(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). The crude reaction product was initially chromatographed on a silica gel column with 2:1 dichloromethane/nhexane as eluent. Fractions containing different Pt(TPC)(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN) regioisomers, all with a  $\lambda_{max}$  of 427 nm, were collected and evaporated to dryness. A second column chromatography was then performed on a neutral alumina column, first with pure dichloromethane to remove the fast-eluting impurities, and then with 4:1 chloroform/dichloromethane, giving a combined yield of 3.59 mg (7.2 %) for the three isomers. PLC with 3:2 dichloromethane/*n*-hexane as eluent was then used to separate the isomers; the top band was identified as  $Pt(TPC)(m-C_6H_4CN)(PhCN)$ , the middle one as the *para* isomer, and the lower one as the *ortho* isomer.

**Pt(TPC)**(*m*-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). Yield 2.1 mg (4.21 %). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon \ge 10^{-4}$  (M<sup>-1</sup>cm<sup>-1</sup>)]: 426 (8.18), 436 (6.70), 501 (0.42), 533 (0.59), 567 (1.15), 595 (2.07). <sup>1</sup>H NMR:  $\delta$  9.08 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz,  $\beta$ -H); 8.92 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz,  $\beta$ -H); 8.72 (broad doublet, 2H,  $\beta$ -H); 8.66 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz,  $\beta$ -H); 8.32 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*o*1); 8.24 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*o*2); 8.10 (overlapping doublets, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 10-*o*1 and 10-*o*2); 7.58-7.82 (m, 8H, overlapping 5,10,15-*m* and 5,15-*p*); 7.48 (dd, 1H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 10-*p*); 6.30 [t, 1H, *p* (PhCN)]; 5.70 [d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz, *p* (C<sub>6</sub>H<sub>4</sub>CN)]; 5.44 [dd, 2H, *m* (PhCN)]; 5.00 [dd, 1H, *m* (C<sub>6</sub>H<sub>4</sub>CN)]; 1.78 [broad doublet, 2H, *o* (PhCN)], 0.68 [d, 1H, *o*2 (C<sub>6</sub>H<sub>4</sub>CN) and s, 1H, *o*1 (C<sub>6</sub>H<sub>4</sub>CN), overlapping]. MS (MALDI-TOF, major isotopomer): M<sup>+</sup> = 923.12 (expt), 923.23 (calcd for C<sub>51</sub>H<sub>32</sub>N<sub>6</sub>Pt).

**Pt(TPC)**(*p*-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). Yield 1.08 mg (2.16 %). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon \ge 10^{-4}$  (M<sup>-1</sup>cm<sup>-1</sup>)]: 426 (3.59), 436 (2.94), 498 (0.27), 528 (0.31), 568 (0.56), 597 (1.11). <sup>1</sup>H NMR:  $\delta$  9.08 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz,  $\beta$ -H); 8.92 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz,  $\beta$ -H ); 8.73 (broad doublet, 2H,  $\beta$ -H); 8.66 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 4 Hz,  $\beta$ -H ); 8.31 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*o*1); 8.24 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 5,15-*o*2); 8.10 (overlapping doublets, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 10-*o*1 and 10 *o*2); 7.83–7.68 (m, 8H, overlapping 5,10,15-*m* and 5,15-*p*); 7.51 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 10-*p*); 6.31 [t, 1H, *p* (PhCN)]; 5.45 [dd, 2H, *m* (PhCN)]; 5.19 [d, 2H, *m* (C<sub>6</sub>H<sub>4</sub>CN)]; 1.79 [broad doublet, 2H, *o* (PhCN)]; 0.57[d, 2H, *o* (C<sub>6</sub>H<sub>4</sub>CN)]. MS (MALDI-TOF, major isotopomer): M<sup>+</sup> = 923.13 (expt), 923.23 (calcd for C<sub>51</sub>H<sub>32</sub>N<sub>6</sub>Pt).

Synthesis and separation of Pt{T(*p*-CH<sub>3</sub>-Ph)C}(*o/m/p*-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). The crude reaction product was initially chromatographed on a silica gel column with 3:1 dichloromethane/*n*-hexane as eluent. Fractions containing different Pt{T(*p*-CH<sub>3</sub>-Ph)C}(*o/m/p*-C<sub>6</sub>H<sub>4</sub>CN)(PhCN) regioisomers, all with a  $\lambda_{max}$  of 427 nm, were collected and evaporated to dryness. A second column chromatography was then performed on a neutral alumina column, first with pure dichloromethane to remove the fast-eluting impurities, and then with pure chloroform, giving a combined yield of 4.17 mg (8.0 %) for the three isomers. PLC with 3:1 dichloromethane/*n*-hexane as eluent was then used to separate the

isomers; the top band was identified as  $Pt{T(p-CH_3-Ph)C}(m-C_6H_4CN)(PhCN)$ , the middle one as the *para* isomer, and the lower one as the *ortho* isomer.

**Pt{T(p-CH<sub>3</sub>-Ph)C}(m-C<sub>6</sub>H<sub>4</sub>CN)(PhCN).** Yield 2.3 mg (4.41 %). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon$  x 10<sup>-4</sup> (M<sup>-1</sup>cm<sup>-1</sup>)]: 427 (5.32), 438 (4.09), 499 (0.27), 529 (0.37), 567 (0.76), 599 (1.60). <sup>1</sup>H NMR: δ 9.06 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.91 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.71 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.65 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.19 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-o1); 8.12 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-o2); 7.98 (overlapping doublets, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 10-o1 and 10-o2); 7.59 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-m1); 7.57 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-m2); 7.51 (overlapping doublets, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 10-o1 and 10-o2); 6.28 [t, 1H, *p* (PhCN)]; 5.70 [d, 1H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, *p* (C<sub>6</sub>H<sub>4</sub>CN)]; 5.42 [dd, 2H, *m* (PhCN)]; 4.99 [dd, 1H, *m* (C<sub>6</sub>H<sub>4</sub>CN)]; 2.68 (s, 6H, 5,15-*p*-CH<sub>3</sub>); 2.65 (s, 3H, 10-*p*-CH<sub>3</sub>); 1.80 [broad doublet, 2H, *o* (PhCN)], 0.70 [d, 1H, o2 (C<sub>6</sub>H<sub>4</sub>CN) and s, 1H, o1 (C<sub>6</sub>H<sub>4</sub>CN)]. MS (MALDI-TOF, major isotopomer): M<sup>+</sup> = 965.17 (expt), 965.28 (calcd for C<sub>54</sub>H<sub>38</sub>N<sub>6</sub>Pt).

**Pt{T(***p***-CH<sub>3</sub>-Ph)C}(***p***-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). Yield 1.17 mg (2.22 %). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): \lambda\_{max} [nm, \varepsilon x 10<sup>-4</sup> (M<sup>-1</sup>cm<sup>-1</sup>)]: 426 (6.27), 439 (4.97), 498 (0.32), 530 (0.49), 567 (1.00), 599 (2.04). <sup>1</sup>H NMR: δ 9.06 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, β-H); 8.92 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, β-H ); 8.72 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, β-H); 8.66 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 4 Hz, β-H ); 8.19 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***o***1-Ph); 8.12 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***o***2-Ph); 7.98 (overlapping doublets, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 10-***o***1-Ph &** *10-o***2-Ph); 7.60 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***m***1-Ph); 7.58 (d, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 5,15-***m***2-Ph); 7.51| (overlapping doublets, 2H, <sup>3</sup>***J***<sub>HH</sub> = 8 Hz, 10-***m***1-Ph & 10***m***2-Ph); 6.28 [t, 1H,** *p* **(PhCN)]; 5.41 [dd, 2H,** *m* **(PhCN)]; 5.19 [dd, 1H,** *m* **(C<sub>6</sub>H<sub>4</sub>CN)]; 2.68 (s, 6H, 5,15-***p***-CH<sub>3</sub>); 2.65 (s, 3H, 10-***p***-CH<sub>3</sub>); 1.78 [brood doublet, 2H,** *o* **(PhCN)], 0.62 [d, 2H,** *o* **(C<sub>6</sub>H<sub>4</sub>CN)]. MS (MALDI-TOF, major isotopomer): M<sup>+</sup> = 965.19 (expt), 965.28 (calcd for C<sub>54</sub>H<sub>38</sub>N<sub>6</sub>Pt).** 

Pt{T(*p*-OCH<sub>3</sub>-Ph)C}(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). The crude reaction product was initially chromatographed on a silica gel column with pure dichloromethane as eluent. Fractions containing different Pt{T(*p*-OCH<sub>3</sub>-Ph)C}(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN) regioisomers, all with a  $\lambda_{max}$  of 427 nm, were collected and evaporated to dryness. A second column chromatography was then performed on a neutral alumina column, first with pure dichloromethane to remove the fast-eluting impurities, and then with pure chloroform,

giving a combined yield of 3.2 mg (6.0 %) for the three isomers. PLC with 3:1 dichloromethane/*n*-hexane as eluent was then used to separate the isomers; the top band was identified as  $Pt{T(p-CH_3-Ph)C}(m-C_6H_4CN)(PhCN)$ , the middle one as a mixture of the *para and meta* isomers, and the lower one as the *ortho* isomer. Because of the very similar  $R_f$  values of the *meta* and *para* isomers, characterization data are only presented for the former.

**Pt{T(p-OCH<sub>3</sub>-Ph)C}(m-C<sub>6</sub>H<sub>4</sub>CN)(PhCN)**. Yield 2.8 mg (5.1 %), UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon$  x 10<sup>-4</sup> (M<sup>-1</sup>cm<sup>-1</sup>)]: 427 (8.17), 440 (6.03), 498 (0.55), 529 (0.68), 567 (1.25), 602 (2.53). <sup>1</sup>H NMR: δ 9.06 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.92 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.71 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.66 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, β-H); 8.23 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-o1-Ph); 8.15 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-o2-Ph); 8.00 (overlapping doublets, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 10-o1-Ph & 10-o2-Ph); 7.35 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-m1-Ph); 7.32 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 5,15-m2-Ph); 7.24 (overlapping doublets, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 10-m1-Ph & 10m2-Ph); 6.29 [t, 1H, p (PhCN)]; 5.69 [d, 1H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, p (C<sub>6</sub>H<sub>4</sub>CN)]; 5.44 [dd, 2H, m (PhCN)]; 5.19 [d, 2H, <sup>3</sup>J<sub>HH</sub> = 4 Hz, p (C<sub>6</sub>H<sub>4</sub>CN)]; 4.99 [dd, 1H, m (C<sub>6</sub>H<sub>4</sub>CN)]; 4.09 (s, 6H, 5,15-p-OCH<sub>3</sub>); 4.06 (s, 3H, 10-p-OCH<sub>3</sub>); 1.80 [brood doublet, 2H, o (PhCN)], 0.70 [d, 1H, o2 (C<sub>6</sub>H<sub>4</sub>CN) and s, 1H, o1 (C<sub>6</sub>H<sub>4</sub>CN)]; 0.64 [d, 2H, o (C<sub>6</sub>H<sub>4</sub>CN)]. MS (MALDI-TOF, major isotopomer): M<sup>+</sup> = 1013.20 (expt), 1013.27 (calcd for C<sub>54</sub>H<sub>38</sub>O<sub>3</sub>N<sub>6</sub>Pt).

General procedure for the synthesis of oxidized Pt{T(p-X-Ph)C}(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) complexes, where X = CF<sub>3</sub>, H, CH<sub>3</sub>, OCH<sub>3</sub>. To a 50-mL roundbottom flask was added 5 mL of dry dichloromethane, a magnetic stirring bar and the Pt{T(p-X-Ph)C}(o/m/p-C<sub>6</sub>H<sub>4</sub>CN)(PhCN) complex (0.0108 mmol) of interest. p-Methylphenylmagnesium bromide solution in diethyl ether (0.108 mL, 0.5M solution in diethyl ether) was added via syringe and the resulting mixture was stirred at room temperature for 2 h. The reaction was judged complete when the original Soret band disappeared and was replaced by a strongly red-shifted one and a weak and broad Q band appeared. The reaction mixture was evaporated to dryness and the resulting solid (with no additional workup) was subjected to column chromatography on a silica gel column with mixed dichloromethane/n-hexane as eluent. The first orange fraction was collected and evaporated to dryness. The product was further purified by PLC with nhexane/dichloromethane as eluent. Overall, a total of five oxidized Pt corroles were synthesized and purified in this manner, with additional details given below.

Pt{T(*p*-CF<sub>3</sub>-Ph)C}(*m*-C<sub>6</sub>H<sub>4</sub>CN)(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). The first column chromatography was carried out with 2:3 dichloromethane/*n*-hexane as an eluent. The eluent for the PLC step was 1:1 dichloromethane/*n*-hexane. Yield: 3.65 mg (30%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon \ge 10^{-4}$  (M<sup>-1</sup>cm<sup>-1</sup>)]: 383 (2.76), 443 (3.91), 723 (0.34). % Elemental analysis: Found: C 58.44, H 2.38, N 6.15; calcd: C 58.12, H 2.80, N 5.92. MS (MALDI-TOF, major isotopomer): (M+H)<sup>+</sup> = 1116.101 (expt), 1116.22 (calcd for C<sub>54</sub>H<sub>31</sub>F<sub>9</sub>N<sub>5</sub>Pt + H).

Pt(TPC)(*m*-C<sub>6</sub>H<sub>4</sub>CN)(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). Both the column chromatography and PLC were carried out with 1:1 dichloromethane/*n*-hexane as eluent. Yield: 7.0 mg (70%). Dark X-ray quality crystals were obtained by slow evaporation of a 1:1 hexane/dichloromethane solution over a period of 15 days, which were successfully analyzed as described below. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon$  x 10<sup>-4</sup> (M<sup>-1</sup>cm<sup>-1</sup>)]: 378 (5.27), 453 (8.29), 722 (0.53). % Elemental analysis: Found: C 67.04; H 3.49; N 7.99; calcd: C 67.17, H 3.76, N 7.68. MS (MALDI-TOF, major isotopomer): (M+H)<sup>+</sup> = 911.99 (expt), 912.25 (calcd for C<sub>51</sub>H<sub>34</sub>N<sub>5</sub>Pt + H).

Pt{T(*p*-CH<sub>3</sub>-Ph)C}(*m*-C<sub>6</sub>H<sub>4</sub>CN)(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). The first column chromatography was carried out with 2:1 dichloromethane/*n*-hexane as an eluent. The eluent for the PLC step was 1:1 dichloromethane/*n*-hexane. Yield: 7.21 mg (70%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon \ge 10^{-4}$  (M<sup>-1</sup>cm<sup>-1</sup>)]: 380 (4.34), 460 (5.82), 725 (0.49). % Elemental analysis: Found: C 67.44, H 3.88; N 7.11; calcd: C 67.98, H 4.23; N 7.34. MS (MALDI-TOF, major isotopomer): (M+H)<sup>+</sup> = 953.99 (expt), 954.30 (calcd for C<sub>54</sub>H<sub>40</sub>N<sub>5</sub>Pt + H).

Pt{T(*p*-CH<sub>3</sub>-Ph)C}(*p*-C<sub>6</sub>H<sub>4</sub>CN)(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) The first column chromatography was carried out with 2:1 dichloromethane/*n*-hexane as an eluent. The eluent for the PLC step was 1:1 dichloromethane/*n*-hexane. Yield: (4.3 mg, 72%). Reddish-brown X-ray quality crystals were grown by slow evaporation of a 1:1 dichloromethane/*n*-hexane solution over a period of 15 days, which were successfully analyzed as described below. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (nm), [ε x 10<sup>-4</sup> (M<sup>-1</sup>cm<sup>-1</sup>)]: 380 (2.80), 460 (3.54), 724 (0.32). % Elemental Analysis: Found: C 67.66, H 4.51; N 7.80; calcd: C 67.98, H 4.23, N 7.34. MS (MALDI-TOF, major isotopomer):  $(M+H)^+ = 953.99$  (expt), 954.30 (calcd for C<sub>54</sub>H<sub>40</sub>N<sub>5</sub>Pt + H).

Pt{T(*p*-OCH<sub>3</sub>-Ph)C}(*m*-C<sub>6</sub>H<sub>4</sub>CN)(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). Both the column chromatography and PLC were carried out with pure dichloromethane as eluent. Yield: 6.4 mg (60%). UVvis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm,  $\varepsilon \ge 10^{-4}$  (M<sup>-1</sup>cm<sup>-1</sup>)]: 385 (7.31), 475 (6.42), 555 (2.06). % Elemental analysis: Found: C 65.25, H 4.36, N 7.11; O, 4.79, Pt, 19.4; calcd: C, 64.73; H, 4.02, N, 6.99. MS (MALDI-TOF, major isotopomer): (M+H)<sup>+</sup> = 1002.16 (expt), 1002.29 (calcd for C<sub>54</sub>H<sub>40</sub>O<sub>3</sub>N<sub>5</sub>Pt + H).

## Discussion of the <sup>1</sup>H NMR spectrum of a representative Pt(IV) complex

The 400 MHz <sup>1</sup>H NMR spectra of the Pt(IV) complexes dissolved in CDCl<sub>3</sub> are consistent with time-averaged  $C_s$  symmetry, as illustrated in Figure 2 for Pt{T(p-CF<sub>3</sub>-Ph)C}(m-C<sub>6</sub>H<sub>4</sub>CN)(PhCN). Thus, the 5- and 15- aryl groups are symmetry-related on the NMR timescale and the  $\beta$ -protons appear as four distinct doublets, each corresponding to 2 H's. The aryl and  $\beta$ -proton signals occur in distinct regions, 7.4–8.3 ppm 8.6–9.1 pmm, respectively, and are thus readily distinguishable. For a given *meso*-aryl group, the two *ortho* (or *meta*) protons give rise to separate signals, because of the asymmetry introduced by the coordinated aryl group (*m*- or *p*-  $C_6H_4CN$ ). Such nonequivalence of ortho (or meta) protons of meso aryl groups have also been observed for five-coordinate iron corroles.<sup>4</sup> The ortho protons of the Pt-bound *m*- or *p*-  $C_6H_4CN$  group are strongly shielded by the aromatic ring current of the corrole and occur at about 0.5-1.0 ppm, facilitating assignments for the rest of the aryl protons. The NMR spectra clearly show the presence of a coordinated, neutral benzonitrile (PhCN) with time-averaged twofold symmetry, whose ortho protons are also strongly shielded, occurring at approximately 1.7–1.8 ppm. Thus, for the Pt(IV) corroles, the <sup>1</sup>H NMR spectra are consistent with the general molecular formula  $Pt{T(p-X-$ Ph)C $(o/m/p-C_6H_4CN)$ (PhCN). As an example, Figure 2 depicts the <sup>1</sup>H NMR spectrum of  $Pt{T(p-CF_3-Ph)C}(m-C_6H_4CN)(PhCN)$ . For each Pt(IV) corrole, the MALDI-TOF mass spectrum also indicates the same formula for the molecular ion. By contrast, ESI mass spectra of the compounds, dissolved in methanol, are consistent with the molecular formula  $Pt{T(p-X-Ph)C}(o/m/p-C_6H_4CN)$  or occasionally  $Pt{T(p-X-Ph)C}(o/m/p-C_6H_4CN)$  $C_6H_4CN$ )(CH<sub>3</sub>OH), indicating loss of the PhCN ligand or its replacement by methanol. DFT calculations (described below) also indicate that the neutral PhCN ligand is labile, consistent with the difficulties (described above) we have experienced with obtaining a relatively disorder-free crystal structure of a Pt(IV) corrole.

<sup>&</sup>lt;sup>4</sup> (a) Steene, E.; Wondimagegn, T.; Ghosh, A. J. Phys. Chem. B, 2001, **105**, 11406-11413. Addition/correction: J. Phys. Chem. B, 2002, **106**, 5312-5312. (b) Zakharieva, O.; Schünemann, V.; Gerdan, M.; Licoccia, S.; Cai, S.; Walker, F. A.; Trautwein, A. X. J. Am. Chem. Soc. 2002, **124**, 6636-6648.



**Figure S1**. Down- and up-field regions of the 400 MHz  $^{1}$ H- $^{1}$ H COSY of Pt{T(*p*-CF<sub>3</sub>-Ph)C}(*m*-C<sub>6</sub>H<sub>4</sub>CN)(PhCN).

# 1D<sup>1</sup>H NMR spectra



**Figure S2**. <sup>1</sup>H NMR spectrum of  $Pt{T(p-CF_3-Ph)C}(m-C_6H_4CN)(PhCN)$ .



**Figure S3**. <sup>1</sup>H NMR spectrum of  $Pt{T(p-CF_3-Ph)C}(p-C_6H_4CN)(PhCN)$ .



**Figure S4**. <sup>1</sup>H NMR spectrum of  $Pt{TPC}(m-C_6H_4CN)(PhCN)$ .



**Figure S5**. <sup>1</sup>H NMR spectrum of  $Pt{TPC}(p-C_6H_4CN)(PhCN)$ .



**Figure S6**. <sup>1</sup>H NMR spectrum of  $Pt{T(p-CH_3-Ph)C}(m-C_6H_4CN)(PhCN)$ .



**Figure 7**. <sup>1</sup>H NMR spectrum of  $Pt{T(p-CF_3-Ph)C}(p-C_6H_4CN)(PhCN)$ .



**Figure S8**. <sup>1</sup>H NMR spectrum of  $Pt{T(p-OCH_3-Ph)C}(m/p-C_6H_4CN)(PhCN)$ . The *m*- and *p*-isomers have very close  $R_f$  values and appear together as a mixture.

## **MALDI-TOF** mass spectra



Figure S9. MALDI-TOF spectrum of  $Pt{T(p-CF_3-Ph)C}(m-C_6H_4CN)(PhCN), M^+ = 1126.82, M^+ (PhCN) = 1024.82, M^+ {(m-NC-Ph)(PhCN)} = 921.81.$ 



Figure S10. MALDI-TOF spectrum of Pt(TPC)(m-C<sub>6</sub>H<sub>4</sub>CN)(PhCN), M<sup>+</sup> = 923.12, M<sup>+</sup>- (PhCN) = 821.08, M<sup>+</sup>- {(m-NC-Ph)(PhCN)} = 719.05



Figure S11. MALDI-TOF spectrum of  $Pt{T(p-CH_3-Ph)C}(m-C_6H_4CN)(PhCN) M^+ = 965.17, M^- (PhCN) = 862.14, M^- {(m-NC-Ph)(PhCN)} = 761.14.$ 



Figure S12. MALDI-TOF spectrum of  $Pt\{T(p-OCH_3-Ph)C\}(m-C_6H_4CN)(PhCN), M^+ = 1013.20, M^+ - (PhCN) = 910.14, M^+ - (m-C_6H_4CN h)(PhCN)\} = 808.10.$ 



**Figure S13**. MALDI-TOF spectrum of  $Pt\{T(p-CF_3-Ph)C\}(m-C_6H_4CN)(p-C_6H_4CH_3), M^+ = 1115.04 \text{ for } C_{54}H_{31}F_9N_5Pt.$ 



**Figure S14**. MALDI-TOF spectrum of Pt(TPC)(m-C<sub>6</sub>H<sub>4</sub>CN)(p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), M<sup>+</sup> = 910.99 for C<sub>51</sub>H<sub>34</sub>N<sub>5</sub>Pt.



**Figure S15**. MALDI-TOF spectrum of  $Pt\{T(p-CH_3-Ph)C\}(m-C_6H_4CN)(p-C_6H_4CH_3), M^+ = 953$  for  $C_{54}H_{40}N_5Pt$ .



**Figure S16**. MALDI-TOF spectrum of  $Pt\{T(p-OCH_3-Ph)C\}(m-C_6H_4CN)(p-C_6H_4CH_3), M^+ = 1001.15$  for  $C_{54}H_{40}O_3N_5Pt$ .



## **High-resolution ESI mass spectra**

**Figure S17**. HR-ESI mass spectrum of  $Pt\{T(p-CF_3-Ph)C\}(m-C_6H_4CN)(PhCN): M^+-(PhCN) = 1024.15$ . Upper panel: experimental spectrum; lower panel: simulation.



**Figure S18**. HR-ESI mass spectrum of  $Pt(TPC)(m-C_6H_4CN)(PhCN)$ :  $M^+-(PhCN) = 820.19$ . Upper panel: experimental spectrum; lower panel: simulation.



**Figure S19**. ESI-Mass spectrum of  $Pt{T(p-CH_3-Ph)C}(m-C_6H_4CN)(PhCN), M^+-(PhCN) = 862.23$ , upper experimental result and lower theoretical simulation.



**Figure S20**. ESI-Mass spectrum of  $Pt{T(p-OCH_3-Ph)C}(m-C_6H_4CN)(PhCN), M^+-(PhCN) = 910.22$ , upper experimental result and lower theoretical simulation.



**Figure S21**. ESI-Mass spectrum of  $Pt\{T(p-CF_3-Ph)C\}(m-C_6H_4CN)(p-C_6H_4CH_3), M^+ = 1115.20$ , upper experimental result and lower theoretical simulation.



**Figure S22**. ESI-Mass spectrum of  $Pt(TPC)(m-C_6H_4CN)(p-C_6H_4CH_3)$ ,  $M^+ = 911.24$ , upper experimental result and lower theoretical simulation.



**Figure S23**. ESI-Mass spectrum of  $Pt{T(p-CH_3-Ph)C}(m-C_6H_4CN)(p-C_6H_4CH_3)$ ,  $M^+ = 953.29$ , upper experimental result and lower theoretical simulation.



**Figure S24**. ESI-Mass spectrum of  $Pt\{T(p-OCH_3-Ph)C\}(m-C_6H_4CN)(p-C_6H_4CH_3), M^+ = 1001.27$ , upper experimental result and lower theoretical simulation.

## **Cyclic voltammograms**



**Figure S25**. Cyclic voltammograms of Cu[T(p-OCH<sub>3</sub>-Ph)C, Au[T(p-OCH<sub>3</sub>-Ph)C], and Pt{T(p-OCH<sub>3</sub>-Ph)C}(m-C<sub>6</sub>H<sub>4</sub>CN)(PhCN) in CH<sub>2</sub>Cl<sub>2</sub> recorded at a scan rate of 100 mV per second.



**Figure S26**. Cyclic voltammograms of Cu[T(p-CF<sub>3</sub>-Ph)C, Au[T(p-CF<sub>3</sub>-Ph)C], and Pt{T(p-CF<sub>3</sub>-Ph)C}(m-C<sub>6</sub>H<sub>4</sub>CN)(PhCN) in CH<sub>2</sub>Cl<sub>2</sub> recorded at a scan rate of 100 mV per second.



**Figure S27**. Cyclic voltammograms of  $Pt{T(p-X-Ph)C}(m-C_6H_4CN)(p-C_6H_4CH_3)$  in CH<sub>2</sub>Cl<sub>2</sub> recorded at a scan rate of 100 mV per second.

#### X-ray structure determinations

Three oxidized Pt corrole derivatives,  $Pt{T(p-CH_3-Ph)C}(p-C_6H_4CN)(p-C_6H_4CH_3)$ ,  $Pt(TPC)(m-C_6H_4CN)(p-C_6H_4CH_3)$ , and  $Pt\{T(p-CH_3-Ph)C\}(m-C_6H_4CN)(p-C_6H_4CH_3)$ , proved amenable to single-crystal X-ray structure analysis, affording definitive proof of platinum insertion into the corrole macrocycle. Diffraction data were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Lab. Samples were mounted on MiTeGen<sup>®</sup> kapton loops and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with an APEXII CCD detector. For the three compounds, diffraction data were collected with synchrotron radiation monochromated using silicon(111) to wavelengths of 0.7749(1) 0.6048(1), and 0.6199(1) Å, respectively. In all cases an approximate full-sphere of data was collected using  $0.3^{\circ} \omega$  scans. The structures were solved by direct methods (SHELXT) and refined by full-matrix least squares on  $F^2$  (SHELXL-2013). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms. Additional crystallographic information has been summarized in Table S1 below and full details can be found in the crystallographic information files provided as the Supporting Information. All structures refined well, giving  $R_1$  [I > 2s(I)] values around 3%. For Pt{T(p-CH<sub>3</sub>-Ph)C $(p-C_6H_4CN)(p-C_6H_4CH_3)$ , the two aryl ligands were disordered. According to the structural model, one side is approximately 66/34 p-C<sub>6</sub>H<sub>4</sub>CN/p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> and the other side is 31/69, suggesting a very slight excess of p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> over p-C<sub>6</sub>H<sub>4</sub>CN in this model. No evidence was found for counterions, either positive or negative, consistent with the Pt<sup>IV</sup>corrole<sup>2–</sup> formulation of the compounds. Thermal ellipsoid plots for the three compounds are given in Figures S4-S6.

	$Pt{T(p-CH_3-Ph)C}(p-$		
	$C_6H_4CN)(p-C_6H_4CH_3)$ -	$Pt(TPC)(m-C_6H_4CN)(p-$	$Pt{T(p-CH_3-Ph)C}(m-$
Sample	$\bullet 0.35C_{6}H_{14}\bullet 0.15CH_{2}Cl_{2}$	$C_6H_4CH_3$ )	$C_6H_4CN)(p-C_6H_4CH_3)$
Chemical formula	C <sub>56.23</sub> H <sub>45.24</sub> N <sub>4.96</sub> Cl <sub>0.31</sub> Pt	$C_{51}H_{34}N_5Pt$	$C_{54}H_{40}N_5Pt$
Formula mass	996.50	911.92	954.00
Crystal system	triclinic	triclinic	triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
$\lambda$ (Å)	0.7749	0.6048	0.6199
<i>a</i> (Å)	10.4746(6)	9.5314(3)	9.5493(9)
<i>b</i> (Å)	11.6239(6)	12.4762(5)	12.9707(13)
<i>c</i> (Å)	18.2464(11)	16.9813(6)	17.3628(17)
$\alpha$ (deg.)	87.752(3)	111.157(2)	106.1050(11)
$\beta$ (deg.)	83.482(3)	97.191(2)	96.8590(12)
γ (deg.)	77.657(3)	90.470(2)	93.6790(12)
Ζ	2	2	2
$V(\text{\AA}^3)$	2156.0(2)	1865.30(12)	2040.7(3)
Temperature (K)	100(2)	100(2)	100(2)
Density $(g/cm^3)$	1.535	1.624	1.553
Measured reflections	77953	61462	142008
Unique reflections	16418	7892	10110
Parameters	592	515	545
Restraints	3	0	0
$R_{\rm int}$	0.033	0.048	0.0169
$\theta$ range (deg.)	2.292 - 36.704	2.672 - 22.500	3.049 - 24.409
$R_1$ , $wR_2$ all data	0.031, 0.073	0.026, 0.064	0.023, 0.053
S (GooF) all data	1.08	1.12	1.17
Max/min res. Dens.	2.09/-1.89	4.12/-1.09	3.87/-1.23
$(e/Å^3)$			

Table S1. Crystallographic data for oxidized Pt corroles.



Figure S28. Thermal ellipsoid plot for  $Pt{T(p-CH_3-Ph)C}(p-C_6H_4CN)(p-C_6H_4CH_3)$ showing the average structure with ellipsoid probabilities at 40%. Both axial ligands are disordered between  $p-C_6H_4CH_3$  over  $p-C_6H_4CN$ . H-atoms and solvent molecules have been omitted for clarity.



Figure S29. Thermal ellipsoid plot for  $Pt(TPC)(m-C_6H_4CN)(p-C_6H_4CH_3)$  with ellipsoid probabilities at 40%. H-atoms and solvent molecules have been omitted for clarity.



Figure S30. Thermal ellipsoid plot for  $Pt{T(p-CH_3-Ph)C}(m-C_6H_4CN)(p-C_6H_4CH_3)$  with ellipsoid probabilities at 40%. H-atoms have been omitted for clarity.

# **BP86-D3/STO-TZ2P** optimized Cartesian coordinates

#### Pt(corrole)(Ph)(PhCN)(Cs)

Pt	-0.522450	0.129548	0.00000
Ν	0.627956	-0.846229	1.254046
N	0.627956	-0.846229	-1.254046
N	1.254389	1.795270	0.00000
N	-1.438855	1.116900	1.449119
N	-1.438855	1.116900	-1.449119
С	0.707453	-0.745571	2.611988
С	0.707453	-0.745571	-2.611988
С	1.616544	-1.634217	0.718158
С	1.616544	-1.634217	-0.718158
С	1.824285	-1.571797	2.988418
С	1.824285	-1.571797	-2.988418
С	2.378142	-2.109856	1.828536
С	2.378142	-2.109856	-1.828536
С	2.381990	1.502455	0.000000
С	3.729576	1.056525	0.00000
С	4.380413	0.809327	1.222163
С	4.380413	0.809327	-1.222163
С	5.683286	0.323346	1.212659
С	5.683286	0.323346	-1.212659
С	6.335574	0.082604	0.00000
С	-0.173817	0.094000	3.329504
С	-0.173817	0.094000	-3.329504
С	-1.161358	0.945783	2.791926
С	-1.161358	0.945783	-2.791926
С	-1.906891	-1.362526	0.00000
С	-2.058377	1.828058	3.498027
С	-2.058377	1.828058	-3.498027
С	-2.369881	-1.869845	1.212510
С	-2.369881	-1.869845	-1.212510
С	-2.432226	2.043434	1.261429
С	-2.432226	2.043434	-1.261429
С	-2.829047	2.491718	2.573629
С	-2.829047	2.491718	-2.573629
С	-2.895372	2.459046	0.00000
С	-3.324913	-2.890702	1.204388
С	-3.324913	-2.890702	-1.204388
С	-3.806766	-3.402790	0.00000
Н	2.166720	-1.738176	4.004547
Н	2.166720	-1.738176	-4.004547
Н	3.242161	-2.762573	1.770016

Н	3.242161	-2.762573	-1.770016
Н	3.846375	0.974876	2.155594
Н	3.846375	0.974876	-2.155594
Н	6.191031	0.124117	2.155401
Н	6.191031	0.124117	-2.155401
Н	7.356480	-0.298860	0.00000
Н	-0.070984	0.110043	4.413469
Н	-0.070984	0.110043	-4.413469
Н	-2.003758	-1.488988	2.163118
Н	-2.003758	-1.488988	-2.163118
Н	-2.088898	1.937744	4.577402
Н	-2.088898	1.937744	-4.577402
Н	-3.594926	3.235192	2.768267
Н	-3.594926	3.235192	-2.768267
Н	-3.687055	-3.283092	2.154904
Н	-3.687055	-3.283092	-2.154904
Н	-3.687572	3.205938	0.00000
Н	-4.551151	-4.199177	0.00000

#### Pt(corrole) $Ph_2$ ( $C_{2v}$ )

Pt	0.000000	0.000000	-0.020701
Ν	0.00000	1.246464	1.486107
Ν	0.00000	1.452382	-1.365160
Ν	0.00000	-1.246464	1.486107
Ν	0.00000	-1.452382	-1.365160
С	0.00000	0.00000	-3.338735
С	0.00000	0.721425	2.741943
С	0.00000	1.266693	-2.722672
С	0.00000	1.842284	3.638074
С	0.00000	2.578184	-3.320553
С	0.00000	2.612948	1.481118
С	0.00000	2.789051	-1.049111
С	0.00000	2.998387	2.870830
С	0.00000	3.324419	0.268160
С	0.00000	3.502627	-2.302622
С	0.00000	-0.721425	2.741943
С	0.00000	-1.266693	-2.722672
С	0.00000	-1.842284	3.638074
С	0.00000	-2.578184	-3.320553
С	0.00000	-2.612948	1.481118
С	0.00000	-2.789051	-1.049111
С	0.00000	-2.998387	2.870830
С	0.00000	-3.324419	0.268160
С	0.00000	-3.502627	-2.302622
С	2.168210	0.000000	-0.010281
С	2.868155	1.205300	0.007309

С	2.868155	-1.205300	0.007309
С	4.267210	1.204149	0.038378
С	4.267210	-1.204149	0.038378
С	4.971039	0.00000	0.053957
С	-2.168210	0.00000	-0.010281
С	-2.868155	1.205300	0.007309
С	-2.868155	-1.205300	0.007309
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С	-4.971039	0.00000	0.053957
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Н	0.00000	1.787367	4.720961
Н	0.00000	2.774609	-4.387249
Н	0.00000	4.018496	3.239152
Н	0.00000	4.411585	0.333264
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Н	0.00000	-1.787367	4.720961
Н	0.00000	-2.774609	-4.387249
Н	0.00000	-4.018496	3.239152
Н	0.00000	-4.411585	0.333264
Н	0.00000	-4.583475	-2.397418
Н	2.346711	2.161058	-0.000805
Н	2.346711	-2.161058	-0.000805
Н	4.802259	2.154730	0.052497
Н	4.802259	-2.154730	0.052497
Н	6.061191	0.00000	0.080101
Н	-2.346711	2.161058	-0.000805
Н	-2.346711	-2.161058	-0.000805
Н	-4.802259	2.154730	0.052497
Н	-4.802259	-2.154730	0.052497
Н	-6.061191	0.00000	0.080101