

# New Bimetallic Reactivity in Pt<sub>2</sub><sup>II,II</sup>/Pt<sub>2</sub><sup>IV,IV</sup> Transformation Mediated by a Benzene Ring

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A new Pt<sub>2</sub><sup>II,II</sup> complex with the formula Pt<sub>2</sub>(TPAB)Me<sub>4</sub> (1), where TPAB = 1,2,4,5-tetrakis(5-(p-C<sub>7</sub>-H<sub>15</sub>Ph)-7-azaindol-1-yl)benzene, has been synthesized. This molecule has excellent solubility in common solvents, which enabled our investigation of its reactions with a variety of oxidants to form Pt<sub>2</sub><sup>IV,IV</sup> species and the reverse reactions of the Pt<sub>2</sub><sup>IV,IV</sup> species back to 1 via reduction. Despite the lack of direct Pt···Pt interactions, the two Pt centers in 1 display distinct bimetallic cooperativity mediated by the central phenyl ring of the TPAB ligand. The most unusual finding is that the reactivity of 1 with MeOTf is highly dependent on the amount of molecular oxygen present in the reaction medium. In the absence of O<sub>2</sub>, the reaction of 1 with MeOTf produced [Pt<sub>2</sub><sup>IV,IV</sup>(TPAB)Me<sub>6</sub>][OTf]<sub>2</sub> (6), while in the presence of O<sub>2</sub>, complex 7, Pt<sub>2</sub><sup>IV,IV</sup>(TPAB)Me<sub>4</sub>(OTf)<sub>2</sub>, was obtained. Compound 1 was found to react readily with O<sub>2</sub> at one atmosphere and ambient temperature to produce an insoluble and not yet fully characterized solid that further reacts with MeOTf to produce 7 quantitatively. NMR and single-crystal X-ray diffraction analyses established that the two Pt<sup>IV</sup> centers in 6 are five-coordinate with a square-pyramidal geometry, while in 7 the two Pt<sup>IV</sup> centers are six-coordinate with an octahedral geometry. Most significantly, the central phenyl ring of the TPAB ligand was transformed to a cyclohexyldienyl in 7, while it remains unchanged in 6. Complex 1 also reacts readily with other oxidants such as CHCl<sub>3</sub>, PhICl<sub>2</sub>, Br<sub>2</sub> (CBr<sub>4</sub>), I<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> to produce Pt<sub>2</sub><sup>IV,IV</sup>(TPAB)Me<sub>4</sub>X<sub>2</sub> (X = Cl, 2; Br, 3; I, 4; OH, 5). The structures of 2–5 are similar to that of 7, showing the generality of the central phenyl ring mediated oxidation of the Pt<sub>2</sub><sup>II,II</sup> system. Complexes 2 and 7 can be reduced and converted back to complex 1 via reactions with BH<sub>4</sub><sup>-</sup>, as established by NMR experiments.

## Introduction

Bimetallic systems<sup>1</sup> have broad applications in transitionmetal-based catalysis, such as activation of small molecules<sup>2</sup> (e.g.,  $O_2$  activation<sup>2b-d</sup> and  $N_2$  fixation<sup>2e,f</sup>), photocatalytical splitting of  $H_2O$ ,<sup>3</sup> and synthesis.<sup>4,5</sup> Many discrete homo- and

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heterobimetallic systems of late transition metals have been developed.<sup>1,3-11</sup> Among previously reported Pt<sub>2</sub> species framed by various bridging ligands,<sup>6-11</sup> the best known is the lantern-shaped compound  $[Pt_2(\mu-pop)_4]^{4-}$  (pop = pyrophosphite,

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 $[P_2O_5H_2]^{2-}$ ), which has a Pt···Pt separation of ~2.93 Å with dinstinct bimetallic cooperativity.<sup>11</sup> Bimetallic cooperativities that confer distinct chemical reactivity or unusual selectivity are largely restricted to species possessing or permitting direct M···M interactions or bonds in previously known examples.<sup>12</sup> In contrast, bimetallic complexes with enforced long M···M separation distances (>6 Å) and distinct bimetallic chemical cooperativities remain rare.<sup>2d,3e,12</sup>

We reported previously a  $Pt_2$  complex,  $Pt_2^{II,II}(TTAB)Me_4$ (TTAB = 1,2,4,5-tetrakis(7-azaindol-1-yl)benzene), that cancleave C–Cl bonds readily at ambient temperature to form a  $Pt_2^{IV}$  species,  $Pt_2^{IV,IV}(\kappa^{3,3}$ -TTAB)Me<sub>4</sub>Cl<sub>2</sub>, with the concomitant dearomatization of the central phenyl ring (Scheme 1).<sup>13a</sup> The unusual reactivity of  $Pt_2^{II,II}$ (TTAB)Me<sub>4</sub> toward C-Cl bonds was attributed to the synergistic effects of the  $Pt_2^{II,II}$  core.<sup>13–15</sup> The two Pt centers in  $Pt_2^{II,II}$  (TTAB)Me<sub>4</sub> are separated by a phenyl ring with a long  $d_{Pt...Pt}$  (6.89 Å) that prohibits direct Pt···Pt interaction or bond formation.<sup>13a</sup> Thus, the Pt<sub>2</sub><sup>II,II</sup>(TTAB)Me<sub>4</sub> complex was a unique example demonstrating bimetallic cooperativity mediated by an aromatic ring. A related  $Pt_2^{II,II}$  system based on a quinoline derivative ligand has been reported recently by Song and coworkers.<sup>13b</sup> One drawback of the previous Pt<sub>2</sub><sup>II,II</sup> systems is their poor solubility in common solvents, which limits the scope of the investigation. To overcome the insolubility of TTAB complexes, we have developed synthetic methods to derivatize the TTAB ligand, and a new ligand, 1,2,4,5-tetrakis(5-(p-C7H15Ph)-7-azaindol-1-yl)benzene (TPAB), has been obtained. In addition to the facile oxidation reactions by C-Cl and C-Br bonds similar to the TTAB Pt<sub>2</sub> complex shown in Scheme 1, the new TPAB Pt<sub>2</sub> complex displays unusual reactivities with MeOTf and oxygen molecules that were not observable for the TTAB complexes. The preliminary findings are reported herein.

### **Results and Discussion**

Syntheses of TPAB and Its  $Pt_2^{II,II}$  Complex 1. The synthetic route to TPAB and its  $Pt_2^{II,II}$  complex (1) is shown in Scheme 2, where 2-aminopyridine serves as a starting material (see Supporting Information for details). Its bromination first gave 3,5-dibromopyridin-2-amine,<sup>16a</sup> which was subsequently cross-coupled with trimethylsilylacetylene to

afford selectively 5-bromo-3-(2-trimethylsilyl)ethynyl)pyridine-2-amine. Treatment of the resultant pyridine substrate successively with KOBu' and HCl (37%) in 'BuOH resulted in 5-bromo-7-azainole.<sup>16b</sup> The subsequent coupling of p-C<sub>7</sub>H<sub>15</sub>PhB(OH)<sub>2</sub> with 5-bromo-7-azainole was realized by using a Buchwald protocol.<sup>16c</sup> Condensation of the resultant 5-(p-C<sub>7</sub>H<sub>15</sub>Ph)-7-azainole with 1,2,4,5-tetrabromobenzene eventually give TPAB as a pale yellow powder in ~12% overall yield. The ligand displacement reaction of TPAB with [PtMe<sub>2</sub>( $\mu$ -SEt<sub>2</sub>)]<sub>2</sub><sup>16d</sup> in THF preceded readily, giving rise to 1 as a yellow solid in 78% yield, which is soluble in most organic solvents including C<sub>6</sub>H<sub>6</sub> and hexanes because of the *p*-Ph-C<sub>7</sub>H<sub>15</sub> moieties.

TPAB and complex 1 have been fully characterized by NMR spectroscopic and elemental analyses. The structure of TPAB determined by X-ray diffraction analysis (see Supporting Information for details) is shown in Figure 1. The <sup>1</sup>H NMR spectrum of 1 shows one set of <sup>1</sup>H signals for all of the unique H atoms, indicating that it has the same structure as that of Pt<sub>2</sub><sup>II,II</sup>(TTAB)Me<sub>4</sub> with  $C_{2h}$  symmetry.

Reactivity of 1 with C-X Bonds, X<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>. Complex 1 reacts readily with 2e<sup>-</sup> oxidants such as C-Cl and C-Br bonds and halogen molecules X<sub>2</sub>. Its reaction with C-Cl bonds is reminiscent of  $Pt_2^{II,II}$  (TTAB)Me<sub>4</sub>,<sup>13a</sup> producing  $Pt_2^{IV,IV}(\kappa^{3,3})$ -TPAB)Me<sub>4</sub>Cl<sub>2</sub> (2), quantitatively. Compound  $\hat{2}$  also can be obtained quantitatively by the reaction of 1 with  $PhI \cdot Cl_2$  in C<sub>6</sub>D<sub>6</sub>. 1 also reacts readily with Br<sub>2</sub> and I<sub>2</sub> in the same manner, producing compounds 3 and 4, respectively (Scheme 3). Noteworthy is that excess Br2 tends to brominate the C3 positions of the TPAB 7-azaindolyl moieties in 1. A better way to quantitatively generate 3 is treating 1 with excess CBr<sub>4</sub> in C<sub>6</sub>H<sub>6</sub>. An interesting finding is that treating 1 with H<sub>2</sub>O<sub>2</sub> gives rise to the dihydroxo complex 5, quantitatively (Scheme 3). These new complexes were characterized by NMR spectroscopic and elemental analyses. NMR data confirmed that the core in 2-5 is a cyclohexyl-1,4-dienyl moiety (see Supporting Information), similar to that of Pt<sub>2</sub><sup>IV,IV</sup>(TTAB)Me<sub>4</sub>Cl<sub>2</sub>.

The high susceptibility of **1** toward oxidation was also evident from cyclic voltammetric study, which shows an irreversible oxidation peak at  $E^{\rm P} \approx 0.13$  V (vs FeCp<sub>2</sub><sup>+/0</sup>) in DMF (Figure 2), attributable to the oxidation of the Pt(II) centers in **1**. The free ligand TPAB and the related mononuclear Pt(II) complex Pt(1,2-BAB)Me<sub>2</sub> (1,2-BAB = 1,2-bis(7-azaindol-1-yl)benzene)<sup>17</sup> do not display oxidation peaks at such low potentials; thus the CV data provide further support to the cooperativity of the two Pt(II) centers mediated by the central phenyl ring.

**Reactivity of 1 with MeOTf and O<sub>2</sub>.** In addition to the 2e<sup>-</sup> oxidation reactions described above, **1** also undergoes a facile overall 4e<sup>-</sup> oxidation reaction with 2 equiv of MeOTf (OTf = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, triflate) in benzene or THF under N<sub>2</sub> to produce the cationic complex **6**,  $[Pt_2^{IV,IV}(TPAB)Me_6][OTf]_2$ , instantaneously and quantitatively (Scheme 4, path a). Complex **6** was fully characterized by NMR spectroscopic and X-ray diffraction analyses. It should be noted that Pt<sub>2</sub>-(TTAB)Me<sub>4</sub> also reacts with MeOTf, but yields an insoluble yellow product that precludes any structural study.

The crystal structure of **6** shown in Figure 3 contains two five-coordinate  $Pt^{IV}$  centers with a square-pyramidal geometry. Each Pt atom in **6** has a short contact distance

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Figure 1. Structure of TPAB with 50% thermal ellipsoids and labeling scheme. The two orientations of the disordered heptyl group are also shown.

### Scheme 2. Syntheses of Ligand TPAB and Complex 1





Figure 2. CV diagram of 1 showing the oxidation peaks in DMF (vs  $FeCp^{2+/0}$ ) with a scan rate of 75 mV/s.

Scheme 3. Reactivity of 1 toward C-Cl/Br Bonds and X<sub>2</sub> Molecules



(2.53(1) Å) with C(42) of the TPAB phenyl spacer, and the Pt···Pt separation distance is 6.22(1) Å. Five-coordinate

Scheme 4. Reactivity of 1 with MeOTf



 $Pt^{IV}$  species are postulated as key intermediates in Shilov chemistry.<sup>17–22</sup> Despite a handful of examples of such mononuclear species in the literature,<sup>17a,22</sup> complex **6** to our

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Figure 3. X-ray structures of the cation in 6 (top, H atoms except those of the central phenyl ring are omitted for clarity) and the central core of 6 (bottom).



**Figure 4.** <sup>1</sup>H NMR spectrum of complex 7 in  $C_6D_6$ .

knowledge is the first structurally characterized five-coordinate dinuclear Pt<sup>IV</sup> species. Steric protection exerted by the TPAB ligand plays a crucial role in stabilizing the two coordinatively unsaturated Pt<sup>IV</sup> centers. Similar stabilization of mononuclear five-coordinate Pt(IV) complexes has been observed previously.<sup>17a</sup>

Another surprising finding is that TPAB adopts a 1,3-N,N-chelating mode in **6** rather than the expected 1,2-*N*,*N* chelate mode, indicating a chelating mode switching accompanying the **1** to **6** oxidation (Scheme 4, path a). The 1,2-N,N-chelate mode has been observed in the mononuclear five-coordinate  $Pt^{IV}Me_3$  analogue [Pt(1,2-BAB)Me\_3](OTf)^{17a} and the TTAB  $Pt_2^{IV,IV}$  complexes previously.<sup>13,15b</sup> The preferential formation of the 1,3-N,N-chelate isomer of **6** from **1** must involve a Pt–N bond dissociation and reassociation process, but the details are not understood yet.

The most intriguing and unusual reactivity of **1** is its reaction with MeOTf in the presence of  $O_2$  that results in not only complex **6** but also complex **7** (Scheme 4, path b) in benzene. The yield of **7** increases with the increase of the amount of  $O_2$ used. The <sup>1</sup>H NMR spectrum of **7** in  $C_6D_6$  displays a singlet at 5.96 ppm with distinct <sup>3</sup> $J_{Pt-H}$  (36.5 Hz) and <sup>4</sup> $J_{Pt-H}$  (14.5 Hz) coupling satellites that are characteristic of a cyclohexyl-1,4dienyl core (Figure 4).<sup>13a</sup> Single-crystal X-ray diffraction and



**Figure 5.** Diagrams showing the structure of **7** (top, H atoms except those of the central phenyl ring are omitted for clarity) and its central core (bottom).



**Figure 6.** <sup>1</sup>H NMR spectra showing the in situ generation of 7 (top) by treating 1 (bottom) successively with  $O_2$  and MeOTf in  $C_6D_6$ . (a) Pure 1; (b) exposed to 1 atm  $O_2$  for 12 h; (c) exposed to 1 atm  $O_2$  for 3 days; (d) MeOTf added; (e) warmed to 60 °C for 3 min (compare with the spectrum of pure compound 7 in Figure 4).

elemental analyses confirmed that complex 7 is indeed an analogue of 2-5 with a formula of  $Pt_2^{IV,IV}(\kappa^{3,3}-TPAB)Me_4$ -(OTf)<sub>2</sub>, as shown in Figure 5. Each  $Pt^{IV}$  center in 7 has an octahedral geometry, coordinated by two methyls (Pt-C = 2.02(2) Å, on average), two N atoms (Pt-N = 2.11(2) Å, on average), one O atom from OTf (Pt-O = 2.151(16) Å), and one C atom from the cyclohexyldienyl ring (Pt-C(46) = 2.12(2) Å). The Pt···Pt separation distance in 7 is 6.51(1) Å.

It is evident that 7 cannot be produced directly by MeOTf  $S_N^2$  additions or simple radical processes involving Meredicals.<sup>17,21</sup> The unexpected formation of 7 is attributable to  $O_2$  since the same species was not observed under  $O_2$ -free conditions (Scheme 4). Furthermore, because  $O_2$  does not react with MeOTf, the Pt<sub>2</sub> complex 1 must play a role in activating  $O_2$ . To further verify the role of  $O_2$ , the reaction of 1 with  $O_2$  in  $C_6D_6$  was examined by <sup>1</sup>H NMR spectroscopy (Figure 6). Addition of  $O_2$  to the solution of 1 at ambient temperature



**Figure 7.** <sup>1</sup>H NMR spectra showing the clean conversion of 7 by  $[Bu_4N][BH_4]$  to **1** in  $C_6D_6$  at room temperature. (Bottom) Spectrum of 7. (Top) Spectrum recorded 3 min after the addition of  $[Bu_4N][BH_4]$ . For the spectrum of pure complex **1**, see Figure 6a.

causes a gradual formation of a yellow solid that is insoluble in most organic solvents. The formation of the yellow solid is also quantitative according to the disappearance of <sup>1</sup>H NMR signals of 1 after  $\sim$ 3 days (Figure 6, a–c). Although the exact nature of this yellow solid has not been established, elemental analysis indicates that it contains oxygen. In addition, the yellow precipitate reacts readily with excess MeOTf, resulting in a clean and quantitative formation of complex 7, accompanied by the formation of MeOOMe ( $\delta$ : <sup>1</sup>H, 3.63 ppm; <sup>13</sup>C, ~61.6 ppm), identified by NMR (Figure 6, c-e; Figure S14 in Supporting Information), thus suggesting that  $O_2$  is indeed involved in the formation of 7. Recently, Goldberg, Britovsek, and co-workers demonstrated that molecular O2 can directly insert into a Pt<sup>II</sup>-Me bond at room temperature, giving rise to  $Pt^{II}$ –OOMe species.<sup>23</sup> In our system, however, due to the high propensity of the  $Pt_2^{II,II}$  complex 1 toward oxidative transformation to  $Pt_2^{IV,IV}$  and the fact that all Pt–Me bonds in 7 remain intact, direct O2 insertion processes are unlikely involved in the generation of complex 7.

Reductive Conversion of Complexes 7 and 2 to Complex 1. The key feature of the new TPAB  $Pt_2$  system is the excellent solubility of the  $Pt_2^{IV,IV}$  products, which makes it possible for us to study their reduction back to 1. The reduction of 7 in  $C_6D_6$  with metals such as Zn and Mg or insoluble hydride salts NaH and CaH<sub>2</sub> proved ineffective, whereas excess  $[Bu_4N][BH_4]$  converted 7 cleanly back to 1 within minutes at room temperature in  $C_6D_6$ , along with the formation of  $H_2$ (Figure 7). A distinct high-field <sup>1</sup>H signal ( $\delta$ , -20.35 ppm with <sup>1</sup>J<sub>Pt-H</sub>  $\approx$  1464 Hz) attributable to<sup>22</sup> Pt<sup>IV</sup>-H was observed when the reduction was carried out in  $CD_2Cl_2$  at -50 °C (Supporting Information, Figure S16). In a similar manner, the dichloride complex 2 can also be converted back to 1 cleanly in  $C_6D_6$  within ~20 min at room temperature (Supporting Information, Figure S17). These reductions can proceed beyond the stage of complex 1 due to excessive  $BH_4^{-}$ , leading eventually to a dark solution consisting of the free TPAB ligand and metallic Pt in a few days. In the CV diagram of **2**, a reversible reduction peak at -1.88 V (vs FeCp<sub>2</sub><sup>+/0</sup>) was observed, which may be attributed to the reduction of the Pt(IV) centers (see Figure S18 in the Supporting Information).

In summary, a new soluble  $Pt_2^{II,II}$  complex 1 has been obtained. Oxygen molecules have been found to have a distinct impact on the reactivity of 1 with MeOTf and the structure of the  $Pt_2^{IV,IV}$  product obtained. The possibility of reductively converting  $Pt_2^{IV,IV}$  back to  $Pt_2^{II}$  has been demonstrated, which has implications in the potential of this  $Pt_2^{II,II}$ system in catalytic bond activation/functionalization processes such as dechlorination or oxygenation.

#### **Experimental Section**

All reactions were performed under N<sub>2</sub> with the standard Schlenk techniques unless otherwise noted. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. THF, Et<sub>2</sub>O, and hexanes were purified using the solvent purification system (Innovation Technology, Inc.). Deuterated solvents  $C_6D_6$ ,  $CD_2Cl_2$ , and  $THF-d_8$ (Cambridge Isotopes) were dried with CaH2. NMR spectra were recorded on Bruker Advance 300, 400, or 500 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to the residual solvent peaks and have been reported in parts per million (ppm). Cyclic voltammetry was performed using a BAS CV-50 W analyzer with a scan rate of 100 mV/s to 1 V/s and a typical concentration of ~0.003 M in DMF using 0.10 M tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., Delta, British Columbia. High-resolution mass spectra (HRMS) were obtained from a Waters/Micromass GC-TOF EI-MS spectrometer. Synthetic details and characterization data of starting materials for TPAB and complexes 2-5, crystal data for TPAB, 6, and 7, and the details for all NMR experiments are provided in the Supporting Information.

Synthesis of TPAB. 1,2,4,5-Tetrabromobenzene (0.33 g, 0.84 mmol), 5-(p-C<sub>7</sub>H<sub>15</sub>Ph)-7-azaindole (1.1 g, 3.77 mmol), CuI (0.18 g, 0.95 mmol), 1,10-phenanthroline (0.30 g, 1.67 mmol), Cs<sub>2</sub>CO<sub>3</sub> (5.4 g, 16.6 mmol), and DMF (5.0 mL) were mixed together and heated at 170 °C under an N2 atmosphere for 3 days. After the reaction, the mixture was cooled to room temperature and poured into water (80 mL). After extraction with ethyl acetate ( $80 \times 3$  mL), the combined organic layers were washed with water (40 mL  $\times$  2) and then dried with Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography with ethyl acetate/hexanes (1:8) as eluent to give the product as a white solid (0.44 g, 42% yield). Colorless crystals of TPAB were obtained via slow evaporation of its CHCl<sub>3</sub> solution. <sup>1</sup>H NMR (400 MHz, 298.0 K, CDCl<sub>3</sub>) δ: 8.49 (d,  ${}^{4}J = 2.0$  Hz, 4H), 8.43 (s, 2H), 8.04 (d,  ${}^{4}J = 2.0$  Hz, 4H), 7.53 (d,  ${}^{3}J = 8.0$  Hz, 8H), 7.29 (d,  ${}^{3}J = 8.0$  Hz, 8H), 6.99 (d,  ${}^{3}J = 3.6$ Hz, 4H), 6.43 (d,  ${}^{3}J = 3.6$  Hz, 1H), 2.68 (t,  ${}^{3}J = 7.6$  Hz, 8H), 1.68 (m, 8H), 1.39-1.32 (m, 32H), 0.92 (t,  ${}^{3}J = 6.8$  Hz, 12H) ppm.  ${}^{13}C$ NMR δ: 147.84, 143.33, 142.29, 136.91, 133.71, 130.93, 129.73, 129.32, 129.19, 127.53, 127.40, 121.02, 101.72, 35.94, 32.16, 31.85, 29.66, 29.52, 23.01, 14.44 ppm. Anal. Calcd for C<sub>86</sub>H<sub>94</sub>N<sub>8</sub>: C 83.32, H 7.64, N 9.04, Found: C 82.78, H 7.58, N 8.94.

Synthesis of Pt<sub>2</sub>(TPAB)Me<sub>4</sub> (1). TPAB (0.15 g, 0.12 mmol) and [PtMe<sub>2</sub>( $\mu$ -SEt<sub>2</sub>)]<sub>2</sub> (0.075 g, 0.12 mmol) were combined in THF (8 mL) to afford a clear solution. The mixture was stirred vigorously under N<sub>2</sub> for 2 days at ambient temperature, resulting in a yellow solution. After removal of the solvent under reduced pressure, the residue was washed with dry Et<sub>2</sub>O/hexanes (1:2) mixed solvents (0.5 mL × 3) to give the product **1** as a yellow power (78% yield). <sup>1</sup>H NMR (500 MHz, 298.0 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 9.42 (d, <sup>4</sup>J = 2.0 Hz, 4H), 7.78 (d, <sup>3</sup>J = 3.5 Hz, 4H), 7.57 (d, <sup>4</sup>J = 2.0 Hz, 4H), 7.33 (d, <sup>3</sup>J = 8.0 Hz, 8H), 7.15 (d, <sup>3</sup>J = 8.0 Hz, 8H), 6.77 (s, 2H), 6.27 (d, <sup>3</sup>J = 3.5 Hz, 4H), 2.62 (t, <sup>3</sup>J = 7.0 Hz, 12H) ppm.

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 $^{13}\text{C}$  NMR & 148.52, 144.44, 142.46, 138.83, 135.79, 132.10, 131.99, 131.77, 129.47, 127.77, 127.36, 103.17, 36.08, 32.40, 32.00, 29.80, 29.78, 23.26, 14.52, -20.87 ppm. Anal. Calcd for  $C_{90}H_{106}N_8Pt_2$ : C 63.96, H 6.32, N 6.63. Found: C 63.40, H 6.05, N 6.35.

Synthesis of Pt<sub>2</sub>(TPAB)Me<sub>4</sub>Cl<sub>2</sub> (2). Complex 1 (24 mg, 0.014 mmol) was dissolved with dry CHCl<sub>3</sub> (0.5 mL) in a test tube in a drybox, resulting in the immediate formation of complex 2. After evaporation of the solvent, the residue was washed with acetone to give complex 2 as a white powder in 96% isolated yield. <sup>1</sup>H NMR (400 MHz, 343.0 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 10.69 (s, 2H), 9.25 (s, 2H), 8.39 (d, <sup>3</sup>J = 3.2 Hz, 2H), 7.71 (d, <sup>3</sup>J = 3.6 Hz, 2H), 7.65 (s, 2H), 7.52 (d, <sup>3</sup>J = 8.0 Hz, 4H), 7.36 (d, <sup>3</sup>J = 8.0 Hz, 4H), 7.13 (d, <sup>3</sup>J = 8.0 Hz, 8H), 6.51 (d, <sup>3</sup>J = 3.2 Hz, 2H), 6.32 (s, with satellites, <sup>3</sup>J<sub>Pt-H</sub> = 21.5 Hz, <sup>4</sup>J<sub>Pt-H</sub> = 8.2 Hz, 2H), 6.24 (d, <sup>3</sup>J = 2.6 Hz, 2H), 2.02 (m) 1.08 (m) 1 3.6 Hz, 2H), 2.62 (m, 8H), 1.98 (s, with satellites,  ${}^{2}J_{Pt-H} = 72.8$ Hz, 6H for Pt-Me), 1.94 (s, with satellites,  ${}^{2}J_{Pt-H} = 72.4$  Hz, 6H for Pt-Me), 1.69 (m, 8H), 1.40 (br, 32H), 1.01 (m, 12H) ppm. <sup>13</sup>C NMR δ: 151.13, 143.10, 142.26, 138.04, 135.72, 135.10, 132.25, 131.67, 130.38, 129.88, 129.81, 129.58, 129.55, 127.83, 127.56, 127.34, 125.30, 123.94, 123.74, 119.08, 105.39, 103.44, 45.77, 36.01, 32.25, 32.22, 31.96, 31.86, 29.74, 29.70, 29.61, 29.60, 23.10, 14.53, 1.44 (Pt-Me), 1.35 (Pt-Me), -3.25 (Pt-Me) ppm. Anal. Calcd for C<sub>90</sub>H<sub>106</sub>N<sub>8</sub>Cl<sub>2</sub>Pt<sub>2</sub>: C 61.39, H 6.07, N, 6.36. Found: C 61.12, H 6.01, N 6.19. Compound 2 can also be obtained by reacting 1 with PhI·Cl<sub>2</sub> (see Supporting Information).

Synthesis of  $[Pt_2(TPAB)Me_6](OTf)_2$  (6). To a yellow  $C_6H_6$ (1 mL) solution of Pt<sub>2</sub>(TPAB)Me<sub>4</sub> (12 mg, 0.007 mmol) in a 5 mL test tube was added quickly neat MeOTf (1.9  $\mu$ L, ~2.2 equiv) via micropipet at ambient temperature in a drybox. A yellow suspension was obtained in a few minutes while shaking the solution vigorously. After evaporation of the solvent, the residue was washed with dry Et2O and then dried under reduced pressure to give complex 6 in 93% isolated yield. Crystals of complex 3 were obtained via slow evaporation of its CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>1</sup>H NMR (400 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>) δ: 8.76 (br, 6H), 8.57 (d,  ${}^{4}J = 1.6, 4$ H), 7.66 (d,  ${}^{3}J = 8.0$  Hz, 8H), 7.52 (d,  ${}^{3}J = 3.6$  Hz, 4 H), 7.45 (d,  ${}^{3}J = 8.0$  Hz, 8H), 7.16 (d,  ${}^{3}J = 3.6$  Hz, 4H), 2.78 (t,  ${}^{3}J = 7.6$  Hz, 8H), 2.36 (s, with satellites,  ${}^{2}J_{\text{Pt-H}} =$ 78.8 Hz, 6H for Pt- $Me_{axial}$ ), 1.75 (m, 8H), 1.51–1.20 (m, 32H), 1.00 (s, with satellites,  ${}^{2}J_{Pt-H} = 68.0$  Hz, 12H for Pt- $Me_{basal}$ ), 1.30 (g,  ${}^{3}J$  = 7.6 Hz, 12H) ppm.  ${}^{13}C$  NMR  $\delta$ : 146.67, 144.53, 140.63, 135.33, 124.25, 134.17, 132.90, 129.87, 127.84, 127.73, 127.29, 126.63, 108.78, 108.29, 35.91, 32.17, 31.87, 29.63, 29.51, 23.00, 17.88 (satellites,  ${}^{1}J_{\text{Pt}-\text{C}} = 754.6$  Hz, Pt-Me<sub>axial</sub>), 14.20, -4.86 (satellites,  ${}^{1}J_{\text{Pt-C}} = 641.2$  Hz, Pt- $Me_{\text{basal}}$ ) ppm. Anal. Calcd for  $C_{94}H_{112}N_8F_6O_6Pt_2S_2$ : C 55.94, H 5.59, N, 5.55. Found: C 55.68, H 5.45, N 5.38.

Synthesis of  $[Pt_2(TPAB)Me_4(OTf)_2]$  (7). A dry C<sub>6</sub>H<sub>6</sub> solution (3.0 mL) of Pt<sub>2</sub>(TPAB)Me<sub>4</sub> (12 mg, 0.007 mmol) was allowed to stand under one atmosphere of O<sub>2</sub> in a Schlenk tube at ambient temperature for 3 days, yielding a yellow suspension. MeOTf (2.5  $\mu$ L, ~3 equiv) was then added quickly via microsyringe at ambient temperature. After being shaken vigorously for about 10 s, the yellow suspension was warmed to 60 °C for 5 min, resulting in a clear pale yellow solution. A large amount of precipitates was produced upon cooling the solution. After

evaporation of the solvent, the residue was washed with dry Et<sub>2</sub>O and then dried under reduced pressure to give complex **7** as pale white powder in 93% isolated yield. Colorless crystals of complex **7** were obtained via slow evaporation of its C<sub>6</sub>H<sub>6</sub> solution. <sup>1</sup>H NMR (400 MHz, 298.0 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 9.70 (m, 4H), 7.70 (m, 4H), 7.64 (d, <sup>3</sup>J = 1.2 Hz, 2H), 7.60–7.55 (m, 8H), 7.43 (d, <sup>3</sup>J = 3.6 Hz, 2H), 7.22 (d, <sup>3</sup>J = 8.0 Hz, 4H), 7.19 (d, <sup>3</sup>J = 8.0 Hz, 4H), 6.32 (d, <sup>3</sup>J = 3.6 Hz, 2H), 6.26 (d, <sup>3</sup>J = 3.6 Hz, 2H), 5.96 (s, with satellites, <sup>3</sup>J<sub>Pt-H</sub> = 36.5 Hz, <sup>4</sup>J<sub>Pt-H</sub> = 14.5 Hz, 2H), 2.65–2.55 (m, 8H), 2.33 (s, with satellites, <sup>2</sup>J<sub>Pt-H</sub> = 72.4 Hz, 6H for Pt-*Me*), 1.99 (s, with satellites, <sup>2</sup>J<sub>Pt-H</sub> = 76.4 Hz, 6H for Pt-*Me*), 1.70–1.50 (m, 8H), 1.48–1.30 (m, 32H), 1.10–0.90 (m, 12H) ppm. Anal. Calcd for C<sub>92</sub>H<sub>106</sub>N<sub>8</sub>F<sub>6</sub>O<sub>6</sub>Pt<sub>2</sub>S<sub>2</sub>: C 55.58, H 5.37, N 5.64. Found: C 55.68, H 5.43, N 5.60.

X-ray Diffraction Anaylsis. Single crystals of the free ligand TPAB were obtained from a CHCl<sub>3</sub>/hexanes solution, while crystals of complexes 6 and 7 were obtained from benzene/ hexanes solutions. All crystals are marginal sizes. For complex 6 the crystal size is very small. For complex 7 the quality of the crystals is very poor and the diffraction intensity is low, with only about 20% of reflections that have intensity greater than  $2\sigma$ . Data were collected on a Bruker Apex II single-crystal X-ray diffractometer with graphite-monochromated Mo Ka radiation, operating at 50 kV and 30 mA, and at either ambient temperature or 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package (version 5.10) and corrected for absorption effects. All structures were solved by direct methods. All three molecules have a crystallographically imposed inversion center. The crystal lattice of TPAB contains 2 CHCl<sub>3</sub> solvent molecules per molecule of TPAB, which were refined successfully. In addition, one aliphatic chain of TPAB is disordered. The disorder was modeled and refined successfully. The crystal lattices of 6 contain disordered CH<sub>3</sub>CN solvent molecules, which could not be modeled or refined. In addition, the OTf anion in 6 also displays some degree of disorder. Hence, to improve the quality of refinements, contributions from solvent molecules and the anions in the crystal lattice of 6 were removed by using the SQUEEZE routine of the Platon program.<sup>24</sup> One aliphatic chain in the asymmetric unit of 7 shows severe disordering. Due to the lack of sufficient data to model and refine the disorder, some of the C-C distances were fixed using DFIX. Nonetheless, despite our best efforts and repeated data collections, we were not able to obtain better data for complex 7. The crystal structural data presented here are from our best effort. For complexes 6 and 7 not all non-hydrogen atoms were refined anisotropically due to the lack of sufficient data. All hydrogen atoms were calculated and their contributions in structural factor calculations were included.

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**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.