# Study of aerobic oxidation of phenyl Pt<sup>II</sup> complexes (dpms)Pt<sup>II</sup>Ph(L) (dpms = di(2pyridyl)methanesulfonate; L = water, methanol, or aniline)<sup>1</sup>

### Julia R. Khusnutdinova, Peter Y. Zavalij, and Andrei N. Vedernikov

Abstract: Oxidation of phenyl Pt<sup>II</sup> complexes K[(dpms)Pt<sup>II</sup>Ph<sub>2</sub>], 1, (dpms)Pt<sup>II</sup>Ph(MeOH), 2, (dpms)Pt<sup>II</sup>Ph(OH<sub>2</sub>), 3, and methyl  $Pt^{II}$  complex (dpms) $Pt^{II}Me(NH_2Ph)$ , 6, with O<sub>2</sub> in aqueous or methanol solutions under ambient conditions leads to corresponding (dpms)Pt<sup>IV</sup>R(X)OH complexes (R = X = Ph, 7; R = Ph, X = OH, 8; R = Ph, X = OMe, 9; R = Me, X = NHPh; 11; dpms = di(2-pyridyl) methanesulfonate). Complexes 7–9 could be isolated in high yield. Complex 11 as well as its phenyl analogue (dpms)Pt<sup>IV</sup>Ph(NHPh)OH, 10 can be prepared in high yield by oxidation of corresponding  $(dpms)Pt^{II}R(NH_2Ph)$  with  $H_2O_2$  in methanol. Phenyl Pt<sup>II</sup> complexes  $(dpms)Pt^{II}Ph(HX)$  derived from HX = aniline and DMSO, 4 and 5, respectively, are inert toward O<sub>2</sub>. The rate of oxidation of 1–5 with O<sub>2</sub> decreases in the order  $1 > 3 \approx$  $2 \gg 4$ , and 5 is unreactive. Methyl analogues are significantly more reactive compared with their phenyl counterparts. Proposed mechanism of oxidation with O<sub>2</sub> includes formation of anionic species (dpms)Pt<sup>II</sup>R(X)<sup>-</sup> responsible for reaction with dioxygen. Attempts at C-O and C-N reductive elimination from phenyl Pt<sup>IV</sup> complexes 7-10 do not lead to phenyl derivatives PhX at 80-100 °C, consistent with the results of the DFT estimates of corresponding activation barriers,  $\Delta G^0$  exceeding 28 kcal/mol.

Key words: platinum phenyl complexes, oxidation, dioxygen, aqueous solution, mechanism.

Résumé : L'oxydation des complexes phénylés du Pt(II), K[(dpms)Pt<sup>II</sup>Ph<sub>2</sub>], 1, (dpms)Pt<sup>II</sup>Ph(MeOH), 2, (dpms)Pt<sup>II</sup>Ph(OH<sub>2</sub>), **3**, ainsi que du complexe méthylé du Pt(II), (dpms)Pt<sup>II</sup>Me(NH<sub>2</sub>Ph), **6**, effectuée avec de l'oxygène (O<sub>2</sub>), en solutions aqueuses ou méthanoliques et dans des conditions ambiantes, conduit à la formation des dérivés  $(dpms)Pt^{IV}R(X)OH$  correspondents (R = X = Ph, 7; R = Ph, X = OH, 8; R = Ph, X = OMe, 9; R = Me, X = NPh, 11; dpms = di(2-pyridy) méthanesulfonate). Les complexes 7–9 ont été isolés avec des rendements élevés. Le complexe 11 ainsi que son analogue phénylé, (dpms)Pt<sup>IV</sup>Ph(NHPh)OH, 10, peuvent être préparés avec d'excellents rendements par oxydation du (dpms)Pt<sup>II</sup>R(NH<sub>2</sub>Ph) avec du H<sub>2</sub>O<sub>2</sub> dans le méthanol. Les complexes phénylés du Pt(II), (dpms)Pt<sup>II</sup>Ph(HX), dans lesquels X représente l'aniline (5) et le DMSO (6) sont inertes vis-à-vis de l'oxygène. Les vitesses d'oxydation des produits 1-5 par l'oxygène diminuent dans l'ordre  $1 > 3 \approx 2 > 4,5$  (inerte). Les analogues méthylés sont sensiblement plus réactifs que leurs analogues phénylés. Le mécanisme d'oxydation proposé pour l'action de l'oxygène implique la formation d'espèces anioniques (dpms)Pt<sup>II</sup>R(X)<sup>-</sup> qui seraient responsables de la réaction avec le dioxygène. Les essais réalisés entre 80 et 100°C en vue d'effectuer une élimination réductrice C-O et C-N à partir des complexes phénylés 7-10 n'ont pas conduit à la formation de dérivés phénylés, PhX; ces résultats sont en accord avec les résultats d'évaluations, faites à l'aide de la théorie de la densité fonctionnelle (TDF), des barrières d'activation correspondantes,  $\Delta G^0$ , qui seraient supérieures à 28 kcal/mol.

Mots-clés : complexes phénylés du platine, oxydation, dioxygène, solution aqueuse, mécanisme.

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Dedicated to Professor Richard Puddephatt.

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### Introduction

The use of oxygen as the terminal oxidant for selective transition-metal-mediated functionalization of organic substrates is an important practical goal (1). One of the possible approaches to selective aerobic CH functionalization may include a sequence of the following transformations: (i) selective CH activation with a  $Pt^{II}$  complex, (*ii*) aerobic conversion of resulting hydrocarbyl Pt<sup>II</sup> to a Pt<sup>IV</sup> complex, and (iii) reductive elimination of organic products from the Pt<sup>IV</sup> intermediate (Scheme 1).

Recently, we reported facile aerobic dpms-enabled (2) functionalization of alkyl Pt<sup>II</sup> complexes in water leading to methanol (3), methyl ether (4), and olefin oxides (5, 6).

Scheme 1. Aerobic Pt<sup>II</sup>-mediated CH functionalization.



Chart 1. dpms Ligand and derived phenyl Pt<sup>II</sup> complexes.



These transformations include selective aerobic conversion of  $Pt^{II}$  alkyls to isolable  $Pt^{IV}$  hydroxo alkyl complexes with subsequent clean reductive C–O elimination of a functionalized alkane product from a  $Pt^{IV}$  center. A similar reaction sequence might also be probed for aryl Pt derivatives. Aromatic CH activation with PtII (7, 8) complexes is well-established, but oxidation of monohydrocarbyl Pt<sup>II</sup>Ar and diaryl Pt<sup>II</sup>Ar<sub>2</sub> complexes with O<sub>2</sub> was never observed. Slow aerobic oxidation of a mixed alkyl aryl (tmeda)-Pt<sup>II</sup>(Ph)Me complex in methanol was reported but reaction products were not characterized (9). In this work, we present first examples of clean aerobic conversion of an anionic diphenyl Pt<sup>II</sup> and several neutral monohydrocarbyl Pt<sup>II</sup>Ph(HX) complexes to corresponding Pt<sup>IV</sup>Ph derivatives (Chart 1), all enabled by dpms ligand. We also report results of attempted  $C(sp^2)$ –O and  $C(sp^2)$ –N reductive elimination from derived Pt<sup>IV</sup>Ph species in water and (or) some organic solvents.

### **Results and discussion**

## (dpms)Pt<sup>II</sup> Complexes 2-6

Methanol complex (dpms)Pt<sup>II</sup>Ph(MeOH) (2) can be synthesized by reductive elimination of benzene from diphenyl Pt<sup>IV</sup> hydride complex (dpms)Pt<sup>IV</sup>Ph<sub>2</sub>H in methanol at 50 °C (eq. [1]). The latter complex can be prepared by protonation of anionic diphenyl Pt<sup>II</sup> species K[(dpms)Pt<sup>II</sup>Ph<sub>2</sub>], 1 (2). Due to the poor solubility of the hydride, elevated temperatures and a prolonged time (5 h) are required to bring reaction to completion. In contrast to (dpms)Pt<sup>IV</sup>Ph<sub>2</sub>H, the methanol adduct **2** is soluble in warm MeOH. As a result, the reaction endpoint can be readily recognized when the entire solid disappears. Other solvento complexes studied in this work, **3**, HX = H<sub>2</sub>O; **4**, HX = PhNH<sub>2</sub>; and **5**, HX = Me<sub>2</sub>SO, can be prepared most conveniently by a ligand exchange between methanol complex **2** and an appropriate ligand HX (eq. [2]; R = Ph).

Fig. 1. ORTEP plots (50% probability ellipsoids) for complexes 4 (*a*) and 11 (*b*).



[1] 
$$(dpms)Pt^{IV}Ph_2H + MeOH$$
  
 $\rightarrow (dpms)Pt^{II}Ph(MeOH) + PhH$ 

$$[2] \qquad (dpms)Pt^{II}R(MeOH) + HX$$

 $\rightarrow$  (dpms)Pt<sup>II</sup>R(HX) + MeOH

For instance, dissolution of 2 in water or DMSO produces quantitatively the corresponding aqua or DMSO adducts. The aniline derivative 4 can be synthesized by reacting 2with 17 equiv. of aniline in methanol solution. Complexes 2and 4 were prepared in an analytically pure form.

All complexes 2–5 were characterized by <sup>1</sup>H NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). Poor solubility of 2–4 in cold methanol or water prevented us from obtaining high quality <sup>13</sup>C NMR spectra. Two sets of signals originating from pyridyl protons could be found in NMR spectra of 2–5, indicating the presence of two non-equivalent pyridyl fragments and a low  $C_1$  molecular symmetry of these complexes. In particular, two readily recognizable most downfield-shifted <sup>1</sup>H NMR signals of pyridyl ortho protons integrating as 1H each could be found in spectra of 2–5 in the range of 8–9 ppm. The signals appear as virtual doublets with characteristic small H–H coupling constant <sup>3</sup>J<sub>HH</sub> = 5–6 Hz.

Complex 4 was characterized by single-crystal X-ray diffraction. X-ray quality crystals of 4 could be obtained by slow crystallization from a reaction mixture. Platinum atom in complex 4 has an idealized square-planar environment (Fig. 1*a*). The Pt1–N15 bond, which is trans to aniline ligand, is 2.024(3) Å long and is shorter than Pt1–N10, 2.102(3) Å, which is trans to phenyl, consistent with a Chart 2. Products of oxidation of complexes 1–4 and 6.



stronger trans influence of the phenyl compared with aniline ligand (10). The Pt1–N21 distance between the metal and the nitrogen atom of the aniline ligand is 2.066(3) Å. Both NH bonds of the aniline ligand point away from the sulfonate group. The shortest Pt1–sulfonate oxygen contact is non-bonding, 3.186 Å.

The mode of coordination of DMSO ligand to the metal in complex **5** could be established by IR spectroscopy. IR spectra of **5** exhibit the presence of the v(S=O) band of S-coordinated DMSO at 1131 cm<sup>-1</sup>, typical for S-coordinated DMSO complexes (11).

Solvento complexes derived from water, **3**, and methanol, **2**, are air-sensitive, whereas aniline derivative **4** and DMSO adduct **5** are stable under air. Reactivity of phenyl (dpms)Pt<sup>II</sup> solvento complexes **2**–**4** toward O<sub>2</sub> will be compared with that of their methyl analogues (dpms)Pt<sup>II</sup>Me(HX) (vide infra) whose aerobic oxidation chemistry was reported recently (HX = H<sub>2</sub>O (3), MeOH (4)). The aniline methyl Pt<sup>II</sup> complex (dpms)Pt<sup>II</sup>Me(NH<sub>2</sub>Ph) (**6**) was unknown and was prepared in this work.

For the preparation of **6**, a procedure similar to that utilized for its phenyl analogue **4** was used (eq. [2]; R = Me). Upon mixing of methanolic solutions of (dpms)Pt<sup>II</sup>Me(MeOH) (4) with 1.2 equiv. of aniline and removal of the solvent, the target compound could be isolated as a colourless solid in 87% yield.

<sup>1</sup>H NMR spectral patterns of **6** in D<sub>2</sub>O are consistent with the  $C_1$  molecular symmetry. The spectrum shows the presence of a Pt<sup>II</sup>Me group resonance at 0.79 ppm ( $J_{195PtH} =$ 72 Hz) integrating as 3H, a singlet of the dpms ligand CH bridge at 5.91 ppm integrating as 1H, a set of partially overlapping signals of the aniline phenyl group, and signals of two non-equivalent pyridyl fragments. Two virtual doublets of ortho H atoms of two pyridyls integrating as 1H each can be observed at 8.14 ppm (J = 5.5 Hz) and 8.73 ppm (J = 5.9 Hz,  ${}^{3}J_{195PtH} = 56$  Hz). ESI-mass spectrum of aqueous solution of **6** shows single  ${}^{195}$ Pt-derived peak with m/z = 553.1 (calculated for (dpms) ${}^{195}$ Pt<sup>II</sup>Me(NH<sub>2</sub>Ph)·H<sup>+</sup>,  $C_{18}H_{20}N_{3}SO_{3}{}^{195}$ Pt, 553.1).

# $(dpms)Pt^{IV}$ Complexes — Oxidation of $(dpms)Pt^{II}R$ complexes with $O_2$ in water or methanol

### Diphenyl complex sym- $(dpms)Pt^{IV}Ph_2(OH)$ (7)

Oxidation of  $K[(dpms)Pt^{II}Ph_2]$  (2) with O<sub>2</sub> in water is facile and is complete in about 2 h at 22 °C. The target com-

Scheme 2. Plausible mechanism of aerobic oxidation of  $(dpms)Pt^{II}$  complexes.



pound, sym-(dpms)Pt<sup>IV</sup>Ph<sub>2</sub>(OH), 7 (Chart 2) is poorly soluble in the reaction medium and can be isolated in an analytically pure form by filtration from the strongly alkaline aqueous solution containing KOH (eq. [3]).

[3] 2 K[(dpms)Pt<sup>II</sup>Ph<sub>2</sub>] + O<sub>2</sub> + 2 H<sub>2</sub>O  

$$\rightarrow$$
 2 sym-(dpms)Pt<sup>IV</sup>Ph<sub>2</sub>(OH) + 2 KOH

Complex 7 dissolved in DMSO- $d_6$  exhibits in its <sup>1</sup>H NMR spectrum a broad singlet at 2.56 ppm with <sup>195</sup>Pt satellites (J = 36 Hz) integrating as 1H and corresponding to the Pt<sup>IV</sup>(OH) proton. A doublet of doublets at 8.30 ppm (J = 5.5, 1.5 Hz) integrating as 2H, which is seen in the most downfield region of the spectrum was assigned to the pyridyl ortho protons. Accordingly, there are nine signals corresponding to two symmetry-related pyridyls and two symmetry-related phenyl ligands in the aromatic region of the <sup>13</sup>C NMR spectrum of 7, evidencing the mirror symmetry of the product.

High reactivity of anionic diphenyl Pt<sup>II</sup> complex 1 toward  $O_2$  in aqueous solution and the retention of the planar arrangement of the four donor atoms at the Pt center upon oxidation of 1 to mirror symmetric 7 are similar to the behaviour of the dimethyl analogue K[(dpms)Pt<sup>II</sup>Me<sub>2</sub>] in its reaction with  $O_2$  (2). Based on the stereochemical outcome of these reactions and also reactions including (dpms)Pt<sup>II</sup>Me(HX), HX = H<sub>2</sub>O (3), L = MeOH (4) and (dpms)Pt<sup>II</sup>(C<sub>2</sub>H<sub>4</sub>OH)OH<sup>-</sup> (5), we suggest that the mechanisms of oxidation of these complexes might be also similar (Scheme 2; X = Me or Ph, steps **b**–**d** only) (5).

The mechanism presented in Scheme 2 was discussed previously (5) and is based on the idea of the axial attack of electrophilic  $O_2$  at  $Pt^{II}$  center (9) that allows to account for the retention of the configuration at the Pt atom in the course of oxidation reaction. At the same time, we presume that in the case of neutral monophenyl complexes (dpms)Pt<sup>II</sup>Ph(HX) only anionic species (dpms)Pt<sup>II</sup>Ph(X)<sup>-</sup> can accept such an attack as it was shown previously for some monoalkyl analogues (5).

Notably, aerobic oxidation of diphenyl  $Pt^{II}$  complexes to form  $Pt^{IV}Ph_2$  products has never been reported. In particular, (tmeda) $Pt^{II}Ph_2$  is unreactive toward  $O_2$ . In contrast, presumably electron-richer mixed-ligand phenyl methyl analogue (tmeda) $Pt^{II}(Ph)Me$  can be oxidized with  $O_2$  (9). Hence, the presence of the pendant axial sulfonate group (see Fig. 1*a*, for example) in anionic (dpms) $Pt^{II}$  species is sufficient to raise energy levels of neutral  $Pt^{II}Ph_2$  fragment and enable

electron transfer between  $Pt^{II}$  atom present in complex 1 and dioxygen (Scheme 2, steps b-c) (5).

## Phenyl dihydroxo complex unsym- $(dpms)Pt^{IV}Ph(OH)_2$ (8)

Solutions of aqua complex **3** in water react slowly with  $O_2$  at atmospheric pressure and ambient temperature to produce colourless unsymmetrical phenyl dihydroxo complex *unsym*-(dpms)Pt<sup>IV</sup>Ph(OH)<sub>2</sub>, *unsym*-**8** (Chart 2), that can be isolated in an analytically pure form in 93% yield (eq. [4]):

[4] 2 (dpms)Pt<sup>II</sup>Ph(OH<sub>2</sub>) + 
$$O_2$$

 $\rightarrow 2 \text{ unsym-(dpms)Pt}^{\text{IV}}\text{Ph}(\text{OH})_2$ 

The presence of two non-equivalent pyridyl groups and hence the  $C_1$  molecular symmetry of *unsym*-**8** are evident from data of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in aqueous and DMSO solutions of *unsym*-**8**. Interestingly, two hydroxo ligands present in this complex give rise to two individual signals that integrate as 1H each and appear as broad singlets at 1.45 ppm (no resolved <sup>195</sup>Pt satellites) and 2.99 ppm (<sup>2</sup>J<sub>195PtH</sub> = 30 Hz). Based on the analogy with complex **7**, the latter signal might be assigned to the proton of the axial OH ligand of complex *unsym*-**8**, whereas the signal at 1.45 ppm might be assigned to the proton of the equatorial OH ligand. Aqueous solutions of **8** acidified with HBF<sub>4</sub> show the presence of monoprotonated species **8**·**H**<sup>+</sup>, *m*/*z* = 556.1 (calculated for (dpms)<sup>195</sup>PtPh(OH)<sub>2</sub>·H<sup>+</sup>, C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>SO<sub>5</sub><sup>195</sup>Pt, 556.1).

The rate of reaction in eq. [4] is much slower than that for  $K[(dpms)Pt^{II}Ph_2]$  (eq. [3]); an estimated half-life of **3** is 8.8 h. This fact may be related to the neutral character of **3** in contrast to anionic complex **1**, and therefore, a much lower fraction of anionic hydrocarbyl (dpms)Pt<sup>II</sup> species is available for attack with O<sub>2</sub> in the case of **3**.

As in the case of bishydrocarbyl complexes  $K[(dpms)Pt^{II}R_2]$ , R = Me or Ph, aerobic oxidation of monohydrocarbyl species (dpms)Pt<sup>II</sup>R(OH<sub>2</sub>) leads to Pt<sup>IV</sup> hydroxo derivatives unsym-(dpms)Pt<sup>IV</sup>R(OH)<sub>2</sub> for both R = Me (3, 5) and Ph. Based on available estimates of half-life of (dpms)Pt<sup>II</sup>R(OH<sub>2</sub>) measured under identical conditions in neutral aqueous solutions at 22 °C, the reactivity of complexes (dpms)Pt<sup>II</sup>R(OH<sub>2</sub>) decreases in the order Me ( $\tau_{1/2} \approx$ 15min) (5) > Ph ( $\tau_{1/2} \approx 8.8$  h). Assuming that mechanisms of these aerobic oxidation reactions are also similar (Scheme 2, steps **a**-**d**), this difference can be related to the electronpoorer character of the phenyl complex 3. On one hand, electron-poorer complex 3 is more acidic than its methyl analogue. That increases the fraction of anionic  $(dpms)Pt^{II}R(OH)^{-}$  species available for reaction with O<sub>2</sub> (5) and makes complex 3 more reactive. On the other hand, an electron-poorer Pt<sup>II</sup> center in anionic intermediate (dpms)Pt<sup>II</sup>Ph(OH)<sup>-</sup> is more difficult to oxidize that leads to an overall lower reactivity of the phenyl aqua complex 3.

Notably, no *mono*phenyl Pt<sup>II</sup> complexes were known that are able to react with  $O_2$  to produce Pt<sup>IV</sup>Ph derivatives. As in the case of complex 1, we assume that the anionic pendant sulfonate tail present in dpms ligand allows to raise energy levels of neutral Pt<sup>II</sup>Ph(OH) fragment to an extent, which is sufficient to enable electron transfer from Pt<sup>II</sup> atom present in this species to  $O_2$ .

Taking these considerations into account, one can suggest that methanol analogue of aqua adduct 3, complex 2 con-

taining an almost equally acidic but more donating methanol ligand will be more reactive toward  $O_2$ . This was proven correct in the experiments described below.

### Phenyl hydroxo methoxo complex (dpms)Pt<sup>IV</sup>Ph(OH)(OMe) (9)

Oxidation of methanol phenyl complex 2 was performed in methanol at ambient temperature. In the course of the reaction, solid complex 2 dissolves to produce a more soluble colourless hydroxo methoxo phenyl complex (dpms)Pt<sup>IV</sup>Ph(OH)(OMe), 9. The product was isolated in analytically pure form in 91% yield (eq. [5]).

[5] 2 (dpms)Pt<sup>II</sup>Ph(MeOH) + 
$$O_2$$

$$\rightarrow 2 \text{ (dpms)Pt}^{IV}Ph(OH)(OMe)$$

According to <sup>1</sup>H NMR spectroscopy, complex **9** in DMSO- $d_6$  exhibits a broad singlet of the Pt<sup>IV</sup>(OH) proton at 2.52 ppm integrating as 1H and a singlet of the methoxo ligand at 2.94 ppm with discernible <sup>195</sup>Pt satellites (<sup>3</sup> $J_{195PtH}$  = 33 Hz) integrating as 3H. An ESI-mass spectrum of solution of **9** in MeOH acidified with HBF<sub>4</sub> shows the presence of a peak with m/z = 570.1 that corresponds to a monoprotonated species (dpms)<sup>195</sup>PtPh(OCH<sub>3</sub>)(OH)·H<sup>+</sup>, (calculated for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>SO<sub>5</sub><sup>195</sup>Pt, 570.1).

Assuming that oxidation of methanol adducts  $(dpms)Pt^{II}R(MeOH)$  proceeds via similar mechanisms for R = Me and Ph and implies retention of the configuration of both R and MeO ligands at the Pt center, complex **9** was tentatively assigned the same configuration (see Chart 2) as the product of aerobic oxidation of the methyl analogue. In the latter case, as established by a single-crystal X-ray diffraction analysis of the reaction product,  $(dpms)Pt^{IV}Me(OMe)OH$  methyl and methoxo fragments retain their positions in the equatorial plane of the product (4).

Half-life of complex **2** (eq. [5]) determined at 22 °C and 1 atm (1 atm = 101.325 kPa) partial pressure of  $O_2$  was estimated to be 5.5 h. This result means that the reactivity of methanolic solutions of **2** is slightly higher than that of aqueous solutions of its aqua-analogue **3**.

A comparison of reactivity of analogous methanol complexes (dpms)Pt<sup>II</sup>R(HX), HX = MeOH, R = Me and Ph shows that the methanol phenyl complex **2** is less reactive compared with the electron-richer methanol methyl complex: Me ( $\tau_{1/2} < 1$  h) (4) > Ph ( $\tau_{1/2} \approx 5.5$  h). The same trend was observed for aqua complexes, HX = H<sub>2</sub>O, R = Me and Ph.

Considering oxidation of the aniline derivatives **4** and **6** with  $O_2$ , one can expect poor reactivity because the acidity of aniline is many orders of magnitude lower than that of  $H_2O$  or MeOH that serve as ligands in species **2** and **3** (12). Hence, anionic intermediates (dpms)Pt<sup>II</sup>R(NHPh)<sup>-</sup> required for oxidation may be available in exceedingly low concentrations only. Similarly, dimethylsulfoxide ligand present in adduct **5** is even less acidic than aniline. Therefore, complex **5** may be even less reactive toward  $O_2$ . Reactivity of aniline adducts **4** and **6** as well as that of DMSO adduct **5** toward  $O_2$  was tested in the following experiments.

### Phenylamido complexes (dpms)Pt<sup>IV</sup>Ph(NHPh)(OH) (10) and (dpms)Pt<sup>IV</sup>Me(NHPh)(OH) (11)

Methanolic solutions of complexes **4** and **5** are inert toward  $O_2$ . No changes were observed by <sup>1</sup>H NMR spectroscopy as well as no new species were detected by ESI-MS after 7 days of exposure of the above solutions to  $O_2$  (1 atm) at ambient temperature.

To be able to test reductive elimination chemistry of an amido phenyl (dpms)Pt<sup>IV</sup>(OH) complex, which can be derived from the aniline adduct **4**, oxidation of **4** was performed with hydrogen peroxide (eq. [6]).

[6] 
$$(dpms)Pt^{II}Ph(PhNH_2) + H_2O_2$$
  
 $\rightarrow (dpms)Pt^{IV}Ph(NHPh)(OH) + H_2O$ 

Treatment of complex **4** dissolved in methanol with 2.5 equiv. of 30% H<sub>2</sub>O<sub>2</sub> produced complex **10** in a quantitative yield, according to <sup>1</sup>H NMR spectroscopy. The colourless product could be precipitated with diethyl ether and isolated in an analytically pure form in 90% yield.

Phenylamido phenyl Pt<sup>IV</sup> complex **10** was fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and ESI-mass spectrometry. <sup>1</sup>H NMR spectrum of **10** in DMSO- $d_6$  solutions shows two broad singlets, one at 3.01 ppm and another at 4.36 ppm integrating as 1H each that can be attributed to OH and NH protons, respectively. Both <sup>1</sup>H and <sup>13</sup>C NMR spectra reveal a low  $C_1$  molecular symmetry of **10**. ESI-mass spectra of **10** dissolved in methanol exhibit single <sup>195</sup>Pt-derived peak at m/z = 631.1 that corresponds to (dpms)<sup>195</sup>PtPh(NHPh)(OH)H<sup>+</sup> (calculated for  $C_{23}H_{22}N_3O_4^{195}Pt$  S, 631.1).

Based on presumed common mechanism of oxidation of  $(dpms)Pt^{II}R(HX)$  species, R = Me and Ph, the configuration of complex **10** at the Pt atom was assumed to be the same as for its methyl analogue **11** (Chart 2; vide infra).

Reactivity of an analogous methyl Pt<sup>II</sup> aniline adduct **6** toward  $O_2$  was also tested. Notably, upon stirring of aqueous solution of **6** under  $O_2$  atmosphere (1 atm) at an ambient temperature, slow oxidation leading to complex (dpms)Pt<sup>IV</sup>Me(NHPh)(OH), **11**, (Chart 2) was evident by <sup>1</sup>H NMR spectroscopy and ESI-mass spectrometry (eq. [7]). The reaction half-life was estimated to be 30 h.

[7] 2 (dpms)Pt<sup>II</sup>Me(PhNH<sub>2</sub>) + O<sub>2</sub>  

$$\rightarrow$$
 2 (dpms)Pt<sup>IV</sup>Me(NHPh)(OH)

Similar to **10**, complex **11** could be prepared by oxidation of methanolic solution of **6** with 1.1 equiv. of  $H_2O_2$ . The reaction is quantitative by NMR spectroscopy.

Aqueous solutions of **11** are weakly basic (pH  $\approx$  9) presumably due to reversible protonation on the nitrogen atom of the phenylamido ligand.

As in the case of phenyl Pt<sup>II</sup> complex **10**, the <sup>1</sup>H NMR spectrum of **11** in DMSO- $d_6$  shows the presence of two broad singlets at 2.22 ppm and 4.17 ppm, corresponding to OH and NH fragments, respectively. Both <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy suggests a low  $C_1$  molecular symmetry of complex **11**. ESI-mass spectra of aqueous solutions **11** exhibit single <sup>195</sup>Pt-derived peak with m/z = 569.1 (calculates for (dpms)<sup>195</sup>PtMe(NHPh)(OH)·H<sup>+</sup>, C<sub>18</sub>H<sub>20</sub>N<sub>3</sub>SO<sub>4</sub><sup>195</sup>Pt, 569.1).

X-ray quality crystals of 11 could be obtained by slow diffusion of ether vapours into solution of 11 in methanol. The structure of complex **11** reveals the presence of a Pt atom in a slightly distorted octahedral environment (Fig. 1*b*). As in the case of the Pt<sup>II</sup>Ph aniline adduct **4**, the Pt1–N2 bond trans to hydrocarbyl is longer than the Pt1–N1 bond trans to phenylamido ligand, 2.189(3) Å vs. 2.089(3) Å, respectively. The Pt1–N3 bond with formally anionic phenylamido ligand is about 0.05 Å shorter than the Pt–N bond in the Pt<sup>II</sup> adduct **4** with neutral aniline ligand, 2.018(3) Å. One of the sulfonate oxygen atoms in the Pt<sup>IV</sup> complex **11** is bound to the metal with a short Pt1–O3 distance of 2.102(3) Å.

The configuration of complex 11 shows that the methyl and phenylamido fragments retain their equatorial positions in the course of oxidation of the  $Pt^{II}$  precursor 6 with  $H_2O_2$ .

Different ability of aniline-derived methyl and phenyl (dpms)Pt<sup>II</sup> complexes **4** and **6** to react with O<sub>2</sub> in water is remarkable. Though the acidity of coordinated aniline may be expected to be many orders of magnitude lower compared with that of Pt<sup>II</sup>-bound water or methanol ligands, corresponding anionic phenylamido Pt<sup>II</sup> species (dpms)Pt<sup>II</sup>R(NHPh)<sup>-</sup> required for reaction with O<sub>2</sub> (Scheme 2, steps **b**–**c**) may still be available in sufficient concentration in the case of R = Me. At the same time, the electron-poorer nature of phenyl ligand might be responsible for precluding a facile electron transfer between the Pt<sup>II</sup> center in (dpms)Pt<sup>II</sup>R(NHPh)<sup>-</sup> and dioxygen.

Finally, the inertness of complex **5** toward  $O_2$  is consistent with its virtual inability to produce an anionic phenyl Pt<sup>II</sup> complex required for aerobic reaction (Scheme 2, step **a**).

# Attempted reductive elimination from (dpms)Pt<sup>IV</sup>Ph complexes

It is assumed that C-X reductive elimination from Pt<sup>IV</sup> center (X = O, N, C, H) is most facile if it proceeds via fivecoordinate intermediates with a coordination vacancy trans to the hydrocarbyl being eliminated (13, 14). The ability of a d<sup>6</sup> metal complex to produce low-coordinate transients and therefore the presence of a good leaving group may be critical for fast reductive elimination chemistry at a  $Pt^{IV}$  center. The best leaving group available in (dpms) $Pt^{IV}$  complexes 7– 11 is the sulfonate but it is cis to hydrocarbyl ligands in all of the complexes. As a result, reductive elimination from 7-11 might be expected to be preceded by their isomerization. Indeed, when alkyl (dpms)Pt<sup>IV</sup>(OH) complexes with an alkyl group cis to the sulfonate are submitted to reductive elimination experiments, intermediates with the alkyl trans to the sulfonate are actual reactive species involved in C-O reductive elimination reactions. These species can be detected by NMR spectroscopy in reaction mixtures and, in a number of cases, isolated in analytically pure form (3–6). Whereas  $C(sp^3)$ –X elimination from  $Pt^{IV}$  can operate an  $S_N 2$ (X = O, N) (15, 16) or a recently discovered direct C(sp<sup>3</sup>)–O elimination mechanism (6), in the case of aryl Pt<sup>IV</sup> derivatives, a direct  $C(sp^2)$ -X elimination was observed only (17). Hence, a direct  $C(sp^2)$ -X reductive elimination from complexes 7-10 might be expected.

Heating complex 7 in DMSO at 100  $^{\circ}$ C for 6 days resulted in clean isomerization to *unsym*-7 featuring one of the phenyl groups in the axial position. No other products were detected in the solution.

Similarly, unsymmetrical phenyl dihydroxo complex 8 dissolved in water and exposed to 100 °C for 3 days cleanly

produced the more stable isomer *sym-***8** with the aryl in the axial position (half-life  $\approx 12.5$  h). No other products were found. The latter complex is  $C_s$  symmetric, according to <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and produces the same signal in ESI-mass spectra as its unsymmetrical precursor.

To probe the effects of solvent and pH on reactivity of *sym-8*, its samples were submitted to C–O reductive elimination in DMSO and also acidic and alkaline aqueous solutions at 100 °C. No changes were detected in these solutions by <sup>1</sup>H NMR spectroscopy after 5 days, suggesting that the Gibbs activation energy for direct C–O elimination from  $Pt^{IV}$  exceeds 30 kcal/mol in all these cases.

Reductive elimination reactions from complexes **9** and **10** were probed in aprotic DMSO- $d_6$ , CD<sub>3</sub>CN, and DMF- $d_7$ .

In the case of **9** in DMSO- $d_6$  solution slow formation of a single Pt<sup>II</sup> complex **5**- $d_6$  and methanol was detected by <sup>1</sup>H NMR spectroscopy and ESI-MS at 100 °C. No anisole or phenol was detected. The reaction was clean and involved presumably the solvent as a reductant (eq. [8]).

[8] 
$$(dpms)Pt^{IV}Ph(OMe)OH + 2 Me_2SO$$
  
 $\rightarrow (dpms)Pt^{II}Ph(dmso) + MeOH + Me_2SO_2$ 

A complex mixture of unidentified products formed in DMF- $d_7$  and CD<sub>3</sub>CN solutions of **9** at 100 °C already after several hours, but no anisole or phenol was detected by <sup>1</sup>H NMR spectroscopy either.

Phenylamido complex **10** in  $CD_3CN$  solution produced a soluble  $Pt^{II}$  complex (dpms) $Pt^{II}Ph(CD_3CN)$  along with a complex mixture of solids of unknown composition after 5 h at 80 °C. No diphenylamine or phenol was detected by <sup>1</sup>H NMR spectroscopy.

Similarly, a complex mixture of products not containing diphenylamine formed when a solution of complex **10** in DMF- $d_7$  was heated at 80 °C for 24 h. ESI-MS spectra of acidified reaction mixtures diluted with methanol exhibited a peak of unreacted starting material, m/z 631.1, and two new peaks with m/z = 1225.2 and m/z = 613.1 that might be assigned to a mono- and doubly-protonated dinuclear species [(dpms)<sub>2</sub>Pt<sup>IV</sup><sub>2</sub>Ph<sub>2</sub>( $\mu$ -NPh)( $\mu$ -NHPh)]<sup>+</sup> (calcd. C<sub>46</sub>H<sub>39</sub>N<sub>6</sub>O<sub>6</sub><sup>195</sup>Pt<sub>2</sub>S2 1225.1) and [(dpms)<sub>2</sub>Pt<sup>IV</sup><sub>2</sub>Ph<sub>2</sub>( $\mu$ -NHPh)<sub>2</sub>]<sup>2+</sup> (calcd. 613.1), respectively.

Therefore, none of complexes 7-10 reacted via Pt<sup>IV</sup>–Ph bond cleavage, and none can be used for arene CH functionalization such as the one shown in Scheme 1. Oxidation of a solvent (complex 9 in DMSO) or, presumably phenylamido ligand (complex 10 in MeCN), or formation of insoluble polynuclear complexes (complex 10 in DMF) was seen instead.

Our DFT estimates of the Gibbs activation energy for the "direct" C–O or C–N elimination from (dpms)Pt<sup>IV</sup>Ph phenyl complexes **8–10** provided high barriers for these reactions. In particular, the Gibbs activation energy for PhOH elimination from *sym-8* is 29.4 kcal/mol. The same value was found for PhOMe elimination from an isomer of complex **9** with phenyl ligand in the axial position. Finally, the Gibbs activation energy for Ph<sub>2</sub>NH elimination from an isomer of complex **10** with the axial Pt<sup>IV</sup>Ph group is 28.7 kcal/mol. Hence,

the results of DFT modeling are qualitatively consistent with our experimental observations.

### Summary

none of the  $\ensuremath{\mathsf{Pt}^{\mathsf{IV}}}$ phenyl Though complexes (dpms)Pt<sup>IV</sup>Ph(X)OH exhibited C-X reductive elimination chemistry in the temperature range of 20-100 °C, results of this study may be important for understanding of factors affecting reactivity of hydrocarbyl Pt<sup>II</sup> complexes toward O<sub>2</sub>. When observed, aerobic oxidation of dipyridylmethanesulfonate monohydrocarbyl  $Pt^{II}$  complexes (dpms) $Pt^{II}R(HX)$ derived from water, methanol, and aniline (HX) leads to  $Pt^{IV}$  hydroxo complexes (dpms) $Pt^{IV}Ph(X)OH$ . This reactivity depends both on the solvento ligand HX and the donicity of the hydrocarbyl R. Among phenyl Pt<sup>II</sup> species, the anionic diphenyl complex is the most reactive, whereas aniline and DMSO adducts are inert:  $X = Ph > MeO \approx HO \gg PhNH$ , DMSO. In turn, methyl derivatives are more reactive than their phenyl counterparts, R = Me > Ph; even the aniline adduct can be oxidized with  $O_2$  when R = Me.

### **Experimental section**

#### General

All manipulations were carried out under purified argon using standard Schlenk and glovebox techniques. All reagents for which synthesis is not given are commercially available from Sigma-Aldrich, Acros, Alfa Aesar, or Pressure Chemicals and were used as received without further purification. Potassium di(2-pyridyl)methanesulfonate was synthesized as described previously (2). DMSO- $d_6$ , CD<sub>3</sub>CN, DMF-d<sub>7</sub>, and CD<sub>3</sub>OD from Cambridge Isotope Laboratories were dried over CaH2, vacuum-transferred, and stored in Teflon-sealed flasks in an argon-filled glovebox. Water was deaerated by repeating freezing-pumping cycles and stored under argon in a Teflon-sealed Schlenk flask in a glovebox. <sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (125 MHz) spectra were recorded on a Bruker AVANCE 400 or Bruker DRX-500 spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer. ESI-MS experiments were performed using a JEOL AccuTOF-CS instrument. Elemental analyses were carried out by Chemisar Laboratories Inc., Guelph, Canada.<sup>3</sup>

#### **Computational details**

Theoretical calculations in this work have been performed using density functional theory (DFT) method (18), specifically functional PBE (19), implemented in an original program package "Priroda" (20). In PBE calculations, relativistic Stevens–Basch–Krauss (SBK) effective core potentials (ECP) (21), optimized for DFT calculations, have been used. Basis set was 311-split for main-group elements with one additional polarization p-function for hydrogen and additional two polarization d-functions for elements of higher periods. Full geometry optimization has been performed without constraints on symmetry. For all species under investigation, frequency analysis has been carried out.

<sup>&</sup>lt;sup>3</sup>Caution: methanol flash point is 12 °C and is lower under pure O<sub>2</sub> atmosphere.

All minima have been checked for the absence of imaginary frequencies. All transition states possessed just one imaginary frequency. Using method of intrinsic reaction coordinate, reactants, products, and the corresponding transition states were proven to be connected by a single minimal energy reaction path.

### Preparation of (dpms)Pt<sup>II</sup>Ph(MeOH) (2)

(dpms)PtPh<sub>2</sub>H (184 mg, 306  $\mu$ mol), prepared according to the literature procedure (2), in MeOH (30 mL) was placed into a 100 mL Schlenk tube equipped with a stirring bar under an argon atmosphere, and the reaction mixture was stirred at 50 °C. Colourless solution formed after 5 h. The solution was filtered under argon, reduced in volume to 2– 3 mL under vacuum, and the resulting suspension was cooled down to –20 °C. White precipitate of **2** was filtered, washed with cold methanol, and dried under vacuum for 12 h. Yield: 127 mg, 75%. White solid, oxidizes in air, poorly soluble in methanol, dissolves in water and DMSO with the loss of methanol ligand and formation of (dpms)PtPh(OH<sub>2</sub>) and (dpms)PtPh(DMSO), respectively.

IR (KBr) v: 3394 (w, br), 3046 (w), 2949 (w), 2764 (w), 1602 (w), 1572 (w), 1480 (w), 1438 (w), 1252 (m), 1168 (m), 1033 (s), 767 (m), 742 (m), 702 (m), 687 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 22 °C)  $\delta$ : 6.02 (s, 1H), 6.86–6.92 (m, 1H), 6.98 (vt, J = 7.5 Hz,), 7.04 (ddd, J = 7.8, 5.7, 1.5 Hz, 1H), 7.43 (dd, J = 7.5, 1.1 Hz, <sup>3</sup> $J_{PtH}$  = 32 Hz, 2H), 7.62 (ddd, J = 7.9, 5.4, 1.6 Hz, 1H), 7.80 (dd, J = 7.9, 1.5 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.98 (td, J = 7.8, 1.6 Hz, 1H), 8.11 (td, J = 7.9, 1.7 Hz, 1H), 8.43 (dd, J = 5.7, 1.7 Hz, 1H), 8.81 (d, J = 5.4 Hz, 1H). <sup>13</sup>C spectrum of (dpms)PtPh(MeOH) could not be obtained due to its low solubility in methanol. ESI of dilute solution in methanol, m/z 554.1. Calculated for (dpms)Pt<sup>II</sup>Ph(MeOH)·H<sup>+</sup>, C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub><sup>195</sup>PtS: 554.1. Anal. found: C, 39.36; H, 3.47; N, 5.19. Calcd. for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>PtS: C, 39.06; H, 3.28; N, 5.06.

### Preparation of (dpms)Pt<sup>II</sup>Ph(OH<sub>2</sub>) (3)

(dpms)PtPh(MeOH) (20 mg, 36  $\mu$ mol) and 20 mL of deaerated water were placed into a 50 mL round-bottomed flask and stirred at room temperature until complete dissolution of the starting material. <sup>1</sup>H NMR spectrum of the sample diluted with D<sub>2</sub>O recorded after 20 min showed complete conversion of **2** into (dpms)PtPh(OH<sub>2</sub>) and 1 equiv. of methanol. The mixture was evaporated to dryness, and the resulting solid was dried under vacuum for 8 h. Yield: 19 mg, 97%. White solid, oxidizes in air, poorly soluble in water.

<sup>1</sup>H NMR (D<sub>2</sub>O, 22 °C)  $\delta$ : 6.08 (s, 1H), 6.98–7.12 (m, 4H), 7.23 (d, J = 7.5 Hz, 2H), 7.63 (ddd, J = 7.7, 5.5, 1.3 Hz, 1H), 7.77 (dd, J = 7.7, 1.5 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 8.01 (td, J = 7.7, 1.6 Hz, 1H), 8.10 (td, J = 7.7, 1.5 Hz, 1H), 8.31 (dd, J = 6.0, 1.5 Hz, 1H), 8.74 (vd, J = 5.5 Hz, 1H). <sup>13</sup>C spectrum of (dpms)PtPh(OH<sub>2</sub>) could not be obtained due to its low solubility in water. ESI of aqueous solution, acidified with HBF<sub>4</sub>, m/z 540.1. Calculated for (dpms)PtPh(OH<sub>2</sub>)·H<sup>+</sup>, C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub><sup>195</sup>PtS: 540.1.

## Preparation of (dpms)Pt<sup>II</sup>Ph(NH<sub>2</sub>Ph) (4)

(dpms)PtPh(MeOH) (65 mg, 117  $\mu$ mol) was placed into a 10 mL vial equipped with a stirring bar. Deaerated methanol (2 mL) and 185 mg of aniline (2 mmol, 17 equiv.) were

added, and a white suspension was stirred at RT. (dpms)PtPh(MeOH) dissolved after 10 min, and the target complex (dpms)PtPh(NH<sub>2</sub>Ph) formed as large crystals. The reaction mixture was placed into a freezer at -20 °C for 4 h. White precipitate of **4** was filtered off, washed with 0.5 mL of cold methanol, and dried under vacuum for 12 h. Yield: 60 mg (97.6 µmol), 83%. White solid, poorly soluble in methanol and water.

IR (KBr) v: 3494 (w, br), 3056 (w), 2828 (w), 1603 (w), 1573 (w), 1494 (w), 1436 (w), 1252 (m), 1222 (m) 1166 (m), 1031 (s), 757 (m), 686 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (D<sub>2</sub>O, 22 °C) & 6.00 (s, 1H), 6.94–7.00 (m, 1H), 7.01–7.16 (m, 6H), 7.20–7.27 (m, 3H), 7.31 (d, J = 7.1 Hz,  ${}^{3}J_{PtH} = 40$  Hz, 2H), 7.77 (vd, J = 7.8 Hz, 2H), 7.89 (td, J = 7.8, 1.4 Hz, 1H), 7.98 (td, J = 7.8, 1.6 Hz, 1H), 8.34 (dd, J = 6.0, 1.4 Hz, 1H), 8.43 (dd, J = 5.6, 1.6 Hz, 1H). <sup>13</sup>C spectrum of (dpms)PtPh(MeOH) could not be obtained due to its low solubility. ESI of solution in MeOH/H<sub>2</sub>O (1:1  $\nu/\nu$ ), m/z 615.1. Calculated for (dpms)PtPh(NH<sub>2</sub>Ph)-H<sup>+</sup>, C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O<sub>3</sub>PtS: C, 44.95; H, 3.44; N, 6.84.

### Preparation of (dpms)Pt<sup>II</sup>Ph(dmso) (5)

(dpms)PtPh(MeOH) (55.6 mg, 100  $\mu$ mol) and 5 mL of dry degassed DMSO were placed into a 25 mL Schlenk tube under an argon atmosphere. The reaction mixture was stirred for 1 h at RT to produce a clear solution. The solvent was removed by vacuum distillation. The resulting solid was washed with cold methanol and ether and dried under vacuum for 24 h at 65 °C. Yield: 51.1 mg, 85%. White solid, soluble in methanol and DMSO. The complex is stable in MeOH solutions at RT for several days; ligand exchange occurs in DMSO- $d_6$  solutions to give (dpms)PtPh(DMSO- $d_6$ ) ( $\tau_{1/2} = 1.2$  h at RT).

IR (KBr) v: 3048 (w), 2924 (w), 1606 (w), 1574 (w), 1483 (w), 1435 (w), 1231 (m), 1167 (m), 1131 (m), 1031 (s), 765 (m), 685 (m) cm<sup>-1</sup>. The v(S=O) band of Scoordinated dimethylsulfoxide at 1131 cm<sup>-1</sup> is missing in IR spectra of other Pt<sup>II</sup> sulfonate complexes reported here. The frequency is typical for Me<sub>2</sub>SO ligand coordinated to a metal through the sulfur atom (11) and similar to S=O frequency of (dpms)Pt(dmso)(OH) (1127 cm<sup>-1</sup>) (6).

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 22 °C)  $\delta$ : 3.07 (s, <sup>3</sup>J<sub>195PtH</sub> = 36 Hz, 3H), 3.19 (s,  ${}^{3}J_{195PtH} = 30$  Hz, 3H), 6.17 (s, 1H), 6.90 (td, J = 7.3, 1.3 Hz, 1H), 7.01 (t, J = 7.3, 1.3 Hz, 1H), 7.17–7.27 (m, 2H), 7.39 (d, J = 7.3,  ${}^{3}J_{195PtH} = 40$  Hz, 1H), 7.58 (ddd, J = 7.9, 5.5, 1.3 Hz, 1H), 7.70 (d, J = 7.3 Hz,  ${}^{3}J_{195PtH} =$ 35 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 8.04 (td, J = 7.9, 1.5 Hz, 1H), 8.12 (td, J = 7.9, 1.5 Hz, 1H), 8.30 (dd, J = 5.5, 1.5 Hz,  ${}^{3}J_{195PtH} = 55$  Hz, 1H), 9.11 (dd, J = 5.5, 1.5 Hz,  ${}^{3}J_{195PtH} = 23$  Hz, 1H).  ${}^{1}$ H NMR (DMSO- $d_{6}$ , 22 °C)  $\delta$ : 3.06 (s,  ${}^{3}J_{195PtH} = 30$  Hz, 3H), 3.09 (s, 3)  ${}^{3}J_{195PtH} = 30$  Hz, 3H), 6.20 (s, 1H), 6.86 (td, J = 7.4, 1.5 Hz, 1H), 6.97 (t, J = 7.4, 1H), 7.16 (td, J = 7.4, 1.5 Hz, 1H), 7.28 (ddd, J = 7.9, 5.5, 1.1 Hz, 1H), 7.35 (d, J = 7.4,  ${}^{3}J_{195PtH} = 30$  Hz, 1H), 7.58 (ddd, J = 7.9, 5.5, 1.1 Hz, 1H), 7.62 (d, J = 7.4,  ${}^{3}J_{195PtH} = 30$  Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 8.06 (td, J = 7.9, 1.4 Hz, 1H), 8.10–8.17 (m, 2H), 8.98 (dd, J = 5.5, 1.4 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 22 °C) δ: 43.8 (CH<sub>3</sub>), 44.4 (CH<sub>3</sub>), 75.4, 124.1, 124.4, 127.3, 128.1 (Cq), 128.2, 129.3, 136.3, 137.3, 140.1,

140.8, 151.5, 152.5 (Cq), 153.2, 154.0 (Cq). Carbon assignments were made from DEPT experiments. ESI of solution in methanol acidified with HBF<sub>4</sub>, m/z 600.1. Calculated for (dpms)PtPh(Me<sub>2</sub>SO)·H<sup>+</sup>, C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub><sup>195</sup>Pt: 600.1. (dpms)PtPh(DMSO-d<sub>6</sub>): ESI of solution in methanol acidified with HBF<sub>4</sub>, m/z 606.1. Calculated for (dpms)PtPh((CD<sub>3</sub>)<sub>2</sub>SO)·H<sup>+</sup>, C<sub>19</sub>H<sub>15</sub>D<sub>6</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub><sup>195</sup>Pt: 606.1.

### Preparation of (dpms)Pt<sup>II</sup>Me(NH<sub>2</sub>Ph) (6)

Solution of (dpms)PtMe(MeOH) (192  $\mu$ mol) in deaerated methanol (10 mL), prepared from isomeric hydrides (dpms)PtMe<sub>2</sub>H (91.4 mg, 192  $\mu$ mol) (5), was placed in a 50 mL Schlenk tube and combined with distilled aniline (18.1 mg; 194  $\mu$ mol, 1.01 equiv.). The mixture was stirred at room temperature for 15 min. According to <sup>1</sup>H NMR, ligand exchange was complete in 15 min. The reaction mixture was evaporated to dryness; the resulting colourless solid was washed with ether and dried under vacuum for 6 h. Yield: 92.9 mg, 87%. White solid, soluble in methanol and water, slowly oxidizes in air.

<sup>1</sup>H NMR (D<sub>2</sub>O, 22 °C) δ: 0.79 (<sup>2</sup> $J_{195PtH}$  = 72 Hz, 3H), 5.91 (s, 1H), 7.05–7.33 (m, 6H), 7.38 (m, 1H), 7.74 (vd, *J* = 7.8 Hz, 2H), 7.88 (vt, *J* = 7.8 Hz, 1H), 8.03 (vt, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 5.5 Hz, 1H), 8.73 (d, *J* = 5.9 Hz, <sup>3</sup> $J_{195PtH}$  = 56 Hz, 1H). ESI-MS of aqueous solution of (dpms)PtMe(NH<sub>2</sub>Ph), *m/z* observed: 553.1. Calcd. for (dpms)PtMe(NH<sub>2</sub>Ph)·H<sup>+</sup>, C<sub>18</sub>H<sub>20</sub>N<sub>3</sub>SO<sub>3</sub><sup>195</sup>Pt: 553.1.

# Preparation of sym-(dpms)Pt<sup>IV</sup>Ph<sub>2</sub>OH (7) by oxidation of K(dpms)Pt<sup>II</sup>Ph<sub>2</sub> (1) with O<sub>2</sub>

K[(dpms)PtPh<sub>2</sub>] (55.9 mg, 88  $\mu$ mol) (2) was dissolved in 2 mL of deaerated water and placed into a 10 mL vial equipped with a magnetic stirring bar. The vial was filled with O<sub>2</sub>, and the solution was stirred at room temperature for 2 h. No K(dpms)PtPh<sub>2</sub> was detected in solution after that time; the solution pH was ~12. White precipitate was filtered off and washed with water until neutral reaction of the filtrate. The product was dried under vacuum for 6 h. Yield: 47.0 mg, 87%. White solid, soluble in dichloromethane and DMSO, insoluble in water.

IR (KBr) v: 3583 (w, br), 3055 (w), 2981 (w), 1604 (w), 1574 (w), 1472 (w), 1449 (w), 1294 (m), 1203 (w), 1143 (s), 1025 (m), 981 (s), 736 (m), 695 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO- $d_6$ , 22 °C)  $\delta$ : 2.56 (br s,  ${}^2J_{195PtH}$  = 36 Hz, 1H), 6.89 (s, 1H), 6.92–7.04 (m, 6H), 7.34 (dd, J = 8.0, 1.7 Hz,  ${}^3J_{195PtH}$  = 30 Hz, 4H), 7.65 (ddd, J = 7.8, 5.5, 1.2 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 8.23 (td, J = 7.8, 1.5 Hz, 2H), 8.30 (dd, J = 5.5, 1.5 Hz, 2H). <sup>13</sup>C NMR (DMSO- $d_6$ , 22 °C)  $\delta$ : 70.7, 124.9, 125.9, 126.4 (Cq), 126.5, 127.3, 130.9, 141.8, 149.6, 151.4 (Cq). Quaternary carbon assignments are from DEPT experiment. ESI of solution in MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) acidified with HBF<sub>4</sub>, m/z 616.1. Calculated for (dpms)PtPh<sub>2</sub>(OH)·H<sup>+</sup>, C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>SO<sub>4</sub><sup>195</sup>Pt: 616.1. Anal. found: C, 44.81; H, 3.45; N, 4.24. Calcd. for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>PtS: C, 44.88; H, 3.27; N, 4.55.

# Preparation of unsym-(dpms)Pt<sup>IV</sup>Ph(OH)<sub>2</sub> (8) by oxidation of (dpms)Pt<sup>II</sup>Ph(OH<sub>2</sub>) with O<sub>2</sub>

(dpms)PtPh(MeOH) (99.1 mg, 179  $\mu$ mol) and 100 mL of deaerated water were placed into 250 mL round-bottomed flask. This suspension was stirred for 30 min under argon.

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Resulting clear solution was stirred under  $O_2$  at room temperature. After 48 h, the solution was reduced in volume to 1 mL under vacuum. Resulting suspension was left at 5 °C for 1 h. White precipitate was filtered off, washed with 0.5 mL of cold water, and dried under vacuum for 8 h. Yield: 92.3 mg, 93%. White solid, very soluble in water, methanol, and DMSO.

IR (KBr) v: 3548 (w, br), 3070 (w), 2928 (w), 1607 (w), 1574 (w), 1481 (w), 1445 (w), 1301 (m), 1210 (w), 1142 (s), 1027 (w), 966 (s), 737 (m), 698 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO $d_6$ , 22 °C)  $\delta$ : 1.45 (br s, 1H), 2.99 (br s,  ${}^2J_{195PtH} = 30$  Hz, 1H), 6.93 (s. 1H), 7.03–7.23 (m, 5H), 7.60 (ddd, J = 7.8, 5.5, 1.3 Hz, 1H), 7.88–8.00 (m, 2H), 8.06 (dd, J = 7.8, 1.3 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 8.26 (td, J = 7.8, 1.5 Hz, 1H), 8.33 (td, J = 7.8, 1.5 Hz, 1H), 8.96 (dd, J = 5.5, 1.5 Hz, 1H). <sup>1</sup>H NMR (D<sub>2</sub>O, 22 °C)  $\delta$ : 6.84 (s, 1H), 7.03 (d, J = 8.0 Hz,  ${}^{3}J_{195PtH} = 20$  Hz, 2H), 7.22–7.35 (m, 3H), 7.58 (ddd, J = 7.9, 5.9, 1.3 Hz, 1H), 7.97 (ddd, J = 7.9, 5.5,1.2 Hz, 1H), 8.03 (dd, J = 5.9, 1.4 Hz, 1H), 8.10 (dd, J =7.9, 1.3 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 8.29 (td, J = 7.9, 1.4 Hz, 1H), 8.35 (td, J = 7.9, 1.4 Hz, 1H), 8.95 (dd, J = 5.5, 1.4 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 22 °C) δ: 70.7, 125.6, 126.2, 126.5, 126.8, 127.1, 127.3 (Cq), 127.6, 132.2, 141.9, 142.7, 148.3, 149.5 (Cq), 151.1, 152.7 (Cq). Quaternary carbon assignments are from DEPT experiment. ESI of solution in MeOH/H<sub>2</sub>O (1:1 v/v) acidified with HBF<sub>4</sub>, m/z 556.1. Calculated for  $(dpms)PtPh(OH)_2 H^+$ ,  $C_{17}H_{17}N_2SO_5^{195}Pt$ : 556.1. Anal. found: C, 36.48; H, 3.29; N, 4.74. Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>PtS: C, 36.76; H, 2.90; N, 5.04.

# Preparation of $(dpms)Pt^{IV}Ph(OMe)(OH)$ (9) by oxidation of $(dpms)Pt^{II}Ph(MeOH)$ with $O_2$

(dpms)PtPh(MeOH) (98.2 mg, 177  $\mu$ mol) in 75 mL of dry methanol was placed into a 250 mL round-bottomed flask equipped with a magnetic stirring bar. The flask was filled with O<sub>2</sub>, and the reaction mixture was stirred vigorously at RT. After 40 h, the clear solution was reduced in volume to ~0.3 mL under vacuum. Resulting suspension was left at -20 °C for 1 h. White precipitate was filtered off, washed with small amount of cold methanol, and dried under vacuum for 12 h. Yield: 91.8 mg, 91%. White solid, soluble in methanol and DMSO.

IR (KBr) v: 3318 (w, br), 3031 (w), 2976 (w), 2817 (w), 1606 (w), 1573 (w), 1483 (w), 1446 (w), 1298 (s), 1210 (m), 1147 (s), 1027 (m), 974 (s), 742 (s), 696 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO- $d_6$ , 22 °C)  $\delta$ : 2.52 (br s, 1H), 2.94 (s,  ${}^{3}J_{195PtH} =$ 33 Hz, 3H), 6.95 (s, 1H), 7.04–7.31 (m, 5H), 7.60 (ddd, J =7.9, 5.8, 1.5 Hz, 1H), 7.92 (dd, J = 5.8, 1.5 Hz, 1H), 7.96 (ddd, J = 7.9, 5.5, 1.2 Hz, 1H), 8.07 (dd, J = 7.9, 1.2 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 8.27 (td, J = 7.9, 1.5 Hz, 1H), 8.34 (td, J = 7.9, 1.5 Hz, 1H), 8.95 (dd, J = 5.5, 1.5 Hz, 1H). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 22 °C)  $\delta$ : 2.66 (s, <sup>3</sup>J<sub>195PtH</sub> = 27 Hz, 3H), 6.67 (s, 1H), 7.10–7.28 (m, 5H), 7.53 (ddd, J = 7.8, 5.5, 1.5 Hz, 1H), 7.92 (ddd, J = 7.8, 5.5, 1.2 Hz, 1H), 8.02-8.14 (m, 3H), 8.24 (td, J = 7.8, 1.5 Hz, 1H), 8.30 (td, J = 7.8, 1.5 Hz, 1H), 9.01 (dd, J = 5.5, 1.5 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 22 °C) δ: 57.3 (CH<sub>3</sub>), 70.7, 125.6, 126.1, 126.3, 126.7, 127.0, 127.8, 129.3 (Cq), 131.4, 141.9, 142.7, 148.0, 149.6 (Cq), 151.5, 152.4 (Cq). Assignments of carbon peaks are made from DEPT experiments. ESI of solution in MeOH acidified with HBF<sub>4</sub>, m/z 570.1. Calculated for (dpms)PtPh(OCH<sub>3</sub>)(OH)·H<sup>+</sup>,  $C_{18}H_{19}N_2SO_5^{195}Pt$ : 570.1. Anal. found: C, 37.79; H, 3.41; N, 4.77. Calcd. for  $C_{18}H_{18}N_2O_5PtS$ : C, 37.96; H, 3.19; N, 4.92.

# Attempted oxidation of $(dpms)Pt^{II}Ph(NH_2Ph)$ (4) and $(dpms)Pt^{II}Ph(dmso)$ (5) with $O_2$

Solution of (dpms)PtPh(NH<sub>2</sub>Ph) (2 mg, 3  $\mu$ mol) in 2 mL of CD<sub>3</sub>OD was placed into a 10 mL round-bottomed flask equipped with a magnetic stirring bar. The flask was filled with oxygen, and the solution was stirred vigorously at room temperature. According to <sup>1</sup>H NMR, the starting material remained unchanged after 7 days. No traces of (dpms)Pt<sup>IV</sup>Ph(NHPh)(OH) or other products were detected in the solution by ESI-MS; no precipitate formed.

An analogous procedure was used for attempted oxidation of (dpms)PtPh(dmso) (2 mg, 3  $\mu$ mol) in CD<sub>3</sub>OD (1 mL) with O<sub>2</sub>. According to <sup>1</sup>H NMR, after 7 days of stirring under O<sub>2</sub> at RT, only starting material (dpms)Pt<sup>II</sup>Ph(dmso) was present in solution; no other products were detected in the amounts exceeding 2%; no precipitate formed.

## Preparation of (dpms)Pt<sup>IV</sup>Ph(NHPh)(OH) (10)

(dpms)PtPh(NH<sub>2</sub>Ph) (53.8 mg, 87.5  $\mu$ mol) and 2 mL of MeOH were placed into a 10 mL vial equipped with a stirring bar, and 25  $\mu$ L of 30% aq. H<sub>2</sub>O<sub>2</sub> were added slowly upon stirring. Stirring continued for 1 h at RT. Solid (dpms)PtPh(NH<sub>2</sub>Ph) dissolved, and reddish solution formed. The yield of **10** is quantitative according to <sup>1</sup>H NMR spectroscopy. Ether (2 mL) was slowly added to the solution, and the resulting mixture was stored for 1 day at RT. Crystalline precipitate of (dpms)PtPh(NHPh)(OH) was filtered off, washed with ether and pentane; yield: 36 mg. An additional fraction of the product was obtained by evaporation of the filtrate. Dry solid was washed with water (10 mL), ether (5 mL), and pentane (5 mL) and dried under vacuum for 10 h; yield: 13.9 mg. Combined yield: 50 mg (79  $\mu$ mol), 90%.

IR (KBr) v: 3555 (w, br), 3050 (w), 2970 (w), 1592 (w), 1574 (w), 1489 (w), 1298 (m), 1207 (w), 1145 (s), 1026 (m), 980 (s), 760 (s), 695 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO- $d_6$ , 22 °C) δ: 3.01 (br s, 1H), 4.36 (br s, 1H), 6.28–6.40 (m, 1H), 6.44– 6.70 (m, 4H), 6.95 (s, 1H), 6.97-7.06 (m, 3H), 7.07-7.27 (m, 2H), 7.59 (ddd, J = 7.8, 5.5, 1.1 Hz, 1H), 7.78–7.84 (m, 1H), 7.97 (d, J = 5.5 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.25 (td, J = 7.8, 1.3 Hz, 1H), 8.29 (td,J = 7.8, 1.3 Hz, 1H), 8.90 (d, J = 4.3 Hz, 1H). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 22 °C) δ: 6.57 (s, 1H), 6.65–6.79 (m, 3H), 6.92 (d, J = 7.8 Hz, 2H), 7.02–7.13 (m, 3H), 7.19 (dd, J = 7.7, 1.9 Hz,  ${}^{3}J_{195PtH} = 23$  Hz, 2H), 7.45–7.54 (m, 2H), 8.03 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 8.08 (d, J =5.8 Hz, 1H), 8.13 (td, J = 7.8, 1.5 Hz, 1H), 8.17 (td, J = 7.6, 1.5 Hz, 1H), 8.60 (d, J = 5.6 Hz, 1H). <sup>13</sup>C NMR (DMSO- $d_6$ , 22 °C) δ: 70.4, 115.6, 118.7, 125.4, 125.8, 126.3, 126.8, 127.2, 127.7, 127.8, 128.2 (Cq), 131.6, 141.8, 142.6, 149.0, 150.0 (Cq), 150.9, 152.1 (Cq), 155.4 (Cq). Quaternary carbon assignments were made based on DEPT experiment. ESI of solution in methanol, m/z 631.1. Calculated for  $C_{23}H_{22}N_3O_4^{195}PtS:$  $(dpms)PtPh(NHPh)(OH) \cdot H^+,$ 631.1. Anal. found: C, 43.52; H, 3.26; N, 6.33. Calcd. for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>PtS: C, 43.81; H, 3.36; N, 6.66.

### Preparation of (dpms)Pt<sup>IV</sup>Me(NHPh)(OH) (11)

Distilled aniline (33.3 mg, 358 µmol, 1.2 equiv.) was added to a solution of (dpms)PtMe(MeOH) prepared from 140.1mg (295 µmol) isomeric hydrides (dpms)PtMe<sub>2</sub>H and 15 mL MeOH (5). According to <sup>1</sup>H NMR, the ligand exchange was complete in 15 min to give (dpms)PtMe(NH<sub>2</sub>Ph), which was used in the next step without isolation. The mixture was placed into an ice bath; 35 mg of 30% H<sub>2</sub>O<sub>2</sub> (~308 µmol) were slowly added to the stirred reaction mixture. Mixture turned yellow immediately after addition of H2O2. According to <sup>1</sup>H NMR, oxidation was complete in less than 15 min to give (dpms)PtMe(NHPh)(OH) quantitatively. The resulting solution was reduced in volume to 2 mL; the product was precipitated with 6 mL of ether, filtered off, and dried under vacuum for 3 h. Yield: 106.2 mg, 63%. The product is soluble in methanol, DMSO, and water; aqueous solutions have weakly basic reaction (pH ~9).

IR (KBr) v: 3548 (w, br), 3087 (w), 2973 (w), 1592 (w), 1489 (w), 1448 (w), 1296 (m), 1212 (m), 1154 (s), 980 (m), 750 (m), 688 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 22 °C) δ: 2.22 (br s, 1H), 4.17 (br s, 1H), 6.40-6.87 (m, 5H), 7.26 (s, 1H), 7.68–7.77 (m, 1H), 7.80 (ddd, J = 7.9, 5.7, 1.2 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 8.23 (td, J =7.9, 1.9 Hz, 1H), 8.30 (td, J = 7.9, 1.2 Hz, 1H), 8.63 (dd, J = 5.7, 1.2 Hz, 1H), 8.67–8.77 (m, 1H). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 22 °C)  $\delta$ : 2.19 (<sup>2</sup> $J_{195PtH}$  = 68 Hz, 3H), 6.49 (s, 1H), 6.82 (m, 1H), 6.90 (m, 2H), 7.07 (d, J = 7.7 Hz, 2H), 7.41 (ddd, J =7.7, 5.8, 1.1 Hz, 1H), 7.77 (ddd, J = 8.0, 5.8, 1.2 Hz, 1H), 7.96 (d, J = 7.7 Hz, 1H), 8.02 (d, J = 7.7 Hz, 1H), 8.07 (td, J = 7.7, 1.5 Hz, 1H), 8.23 (td, J = 7.7, 1.5 Hz, 1H), 8.33 (d, J = 5.8 Hz, 1H), 8.67 (d, J = 5.8 Hz, 1H). <sup>13</sup>C NMR  $(DMSO-d_6, 22 \text{ °C}) \delta: 2.2 (^1J_{195PtC} = 606 \text{ Hz}), 70.4, 116.0,$ 119.4, 125.8, 126.7, 126.9, 128.0, 128.2, 141.5, 142.4, 148.3, 149.7, 150.0, 152.2, 155.8. ESI-MS of aqueous solution of (dpms)PtMe(NHPh)(OH), m/z observed: 569.1. Calcd. for  $(dpms)PtMe(NHPh)(OH) \cdot H^+$ ,  $C_{18}H_{20}N_3SO_4^{195}Pt$ : 569.1. Anal. found: H, 3.24; C, 38.18; N, 6.97; S, 5.50. Calcd. for C<sub>18</sub>H<sub>19</sub>O<sub>4</sub>N<sub>3</sub>PtS, H, 3.37; C, 38.03; N, 7.39; S, 5.64.

### Oxidation of (dpms)Pt<sup>II</sup>Me(NH<sub>2</sub>Ph) (6) with O<sub>2</sub>

(dpms)Pt<sup>II</sup>Me(PhNH<sub>2</sub>) (40 mg, 72 µmol) and 10 mL of water were placed into a 50 mL round-bottomed flask equipped with a magnetic stirring bar. The flask was filled with O<sub>2</sub>, and the solution was stirred vigorously under O<sub>2</sub> atmosphere at room temperature. According to <sup>1</sup>H NMR spectroscopy, slow oxidation occurred to give (dpms)PtMe(NHPh)(OH) as the only Pt<sup>IV</sup> product. The reaction half-life is ~30 h at RT. Signals corresponding to protonated starting material (*m*/*z* 553.1) and oxidation product (dpms)Pt<sup>IV</sup>Me(NHPh)(OH) (*m*/*z* 569.1) were detected by ESI-MS.

# Isomerization of unsym-(*dpms*)Pt<sup>IV</sup>Ph(OH)<sub>2</sub> (unsym-8) into sym-(dpms)Pt<sup>IV</sup>Ph(OH)<sub>2</sub> (sym-8)

Solution of *unsym*-(dpms)PtPh(OH)<sub>2</sub> (103 mg, 180  $\mu$ mol) in water (30 mL) was placed into a 50 mL round-bottomed flask equipped with a magnetic stirring bar and a condenser. The mixture was heated at 100 °C. After 70 h, the reaction mixture was reduced in volume to ~1 mL under vacuum and

Compound	4	11
Formula	$C_{23}H_{21}N_3O_3PtS{\cdot}2CH_3OH$	$C_{18}H_{19}N_3O_4PtS$
FW	678.66	568.51
Crystal system	Monoclinic	Monoclinic
Space group	P2/n	$P2_1/c$
a (Å)	9.9681(6)	8.530(2)
b (Å)	8.7798(5)	11.102(3)
c (Å)	28.8445(16)	19.457(5)
α (°)	90	90
β (°)	90.6590(10)	90.916(4)
γ (°)	90	90
Volume (Å <sup>3</sup> )	2524.2(3)	1842.4(8)
Ζ	4	4
$D_{\text{(calcd.)}}$ (Mg/m <sup>3</sup> )	1.786	2.050
Abs. coeff. (mm <sup>-1</sup> )	5.682	7.759
F(000)	1336	1096
No. of reflns./ind.reflns.	47802/5791	22924/4408
Abs. corr.	Semi-empirical	Semi-empirical
No. of data/restr./params.	5791/31/336	4408/1/267
$RI, wR^2 (I > 2\sigma(I))$	0.0244, 0.0583	0.0231, 0.0588

Table 1. X-ray data for the complexes 4 and 11.

left at 5 °C for 1 h. White precipitate was filtered off and dried under vacuum for 6 h. Yield: 94 mg, 91%.

IR (KBr) v: 3500 (w, br), 3062 (w), 2964 (w), 1607 (w), 1574 (w), 1475 (w), 1441 (w), 1267 (m), 1205 (m), 1146 (s), 996 (m), 736 (m), 691 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO- $d_6$ , 22 °C)  $\delta$ : 2.32 (br s, <sup>2</sup> $J_{195PtH}$  = 26 Hz, 2H), 6.38 (d, J = 7.3 Hz, <sup>3</sup> $J_{195PtH}$  = 35 Hz, 2H), 6.74 (s, 1H), 6.87 (vt, J = 7.3 Hz, 2H), 7.04 (vt, J = 7.3 Hz, 1H), 7.65 (ddd, J = 7.8, 5.8, 1.3 Hz, 2H), 8.06 (d, J = 5.8 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 8.31 (td, J = 7.8, 1.3 Hz, 2H). <sup>1</sup>H NMR (D<sub>2</sub>O, 22 °C)  $\delta$ : 6.72 (s, 1H), 6.85–7.22 (m, 4H), 7.26 (vt, J = 7.3 Hz, 1H), 7.63 (ddd, J = 8.0, 5.9, 1.3 Hz, 2H), 8.09 (dd, J = 5.9, 1.4 Hz, 2H). <sup>8.14</sup> (dd, J = 8.0, 1.3 Hz, 2H), 8.33 (td, J = 8.0, 1.4 Hz, 2H). <sup>13</sup>C NMR (DMSO- $d_6$ , 22 °C)  $\delta$ : 72.1, 125.9, 126.3, 127.2, 127.4, 128.0, 132.5, 142.3, 149.8, 150.9.

### Attempted reductive elimination from *sym*-(dpms)Pt<sup>IV</sup>Ph<sub>2</sub>(OH) (*sym*-7) in DMSO-*d*<sub>6</sub> solution

A sample of *sym*-(dpms)PtPh<sub>2</sub>(OH) (2 mg, 3.2 µmol) was dissolved in dry DMSO- $d_6$  (0.7 mL), and solution was placed into an NMR Young tube under an argon atmosphere. The Young tube was heated at 100 °C in a silicon-oil bath. The only reaction observed was isomerization of **7** into corresponding unsymmetrical isomer (half-life is 26 h). After 6 days, the isomerization was complete, yield of *unsym*-**7** > 97% by <sup>1</sup>H NMR spectroscopy. No biphenyl or phenol were detected.

<sup>1</sup>H NMR (DMSO- $d_6$ , 22 °C)  $\delta$ : 1.37 (br s, 1H), 6.65 (d, J = 8.2 Hz,  ${}^3J_{195PtH} = 44$  Hz, 2H), 6.78 (s, 1H), 6.88–7.12 (m, 6H), 7.20–7.39 (m, 2H), 7.59 (ddd, J = 7.9, 5.9, 1.5 Hz, 1H), 7.65 (ddd, J = 7.9, 5.7, 1.3 Hz, 1H), 8.00 (dd, J = 5.7, 1.5 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 8.14 (dd, J = 7.9, 1.5 Hz, 1H), 8.20 (dd, J = 5.9, 1.5 Hz, 1H), 8.25 (td, J = 7.9, 1.5 Hz, 1H), 8.34 (td, J = 7.9, 1.5 Hz, 1H). <sup>13</sup>C NMR (DMSO- $d_6$ , 22 °C),  $\delta$ : 71.9, 124.3, 125.1, 125.5, 125.8, 126.9, 127.1, 127.3, 127.4, 128.4, 128.7, 132.7, 133.8, 141.6, 142.6, 148.7, 150.3, 152.7, 152.9.

## Attempted reductive elimination from *sym*-(dpms)Pt<sup>IV</sup>Ph(OH)<sub>2</sub> (*sym*-8)

Four samples of sym-(dpms)PtPh(OH)<sub>2</sub> (2.5 mg each, 4.5 µmol) were dissolved in neutral D<sub>2</sub>O (0.8 mL), 50 mmol/L solution of HBF<sub>4</sub> in D<sub>2</sub>O (0.8 mL), 11 mmol/L NaOD/D<sub>2</sub>O solution (0.8 mL), and DMSO- $d_6$  (0.8 mL) under argon. The solutions were placed into NMR Young tubes and Teflon-sealed. Residual solvent peaks were used as internal standards. The solutions were heated at 100 °C. According to <sup>1</sup>H NMR spectroscopy, concentration of *sym*-(dpms)PtPh(OH)<sub>2</sub> remained unchanged after 5 days; no products were detected by <sup>1</sup>H NMR.

## Attempted reductive elimination from (dpms)Pt<sup>IV</sup>Ph(OH)(OMe) (9)

### Reaction in DMSO-d<sub>6</sub>

A sample of (dpms)PtPh(OMe)(OH) (2 mg, 3.5 µmol) was dissolved in 0.7 mL of DMSO- $d_6$ . The solution was placed into an NMR Young tube and Teflon-sealed under argon. The solution was heated at 80-100 °C, periodically cooled down to room temperature and analyzed by <sup>1</sup>H NMR. Slow reaction occurred at 80 °C with a half-life of ~47 h. The reaction continued at 100 °C with a half-life of 4.5 h; quantitative formation of only one platinum-containing product, (dpms)PtPh(DMSO- $d_6$ ), was observed. <sup>1</sup>H NMR of the product was identical to that of  $(dpms)PtPh(DMSO-d_6)$  obtained by dissolving (dpms)Pt(MeOH) in DMSO-d<sub>6</sub>; ESI of acidified solution diluted with methanol showed the presence of a signal with m/z = 606.1 (calcd. For (dpms)PtPh(C<sub>2</sub>D<sub>6</sub>SO)H<sup>+</sup>,  $C_{19}H_{15}D_6N_2S_2O_4^{195}Pt$ , m/z 606.1). One equivalent of methanol was released into solution, according to <sup>1</sup>H NMR spectroscopy.

#### Reactions in DMF- $d_7$ and CD<sub>3</sub>CN

Analogous procedure was applied to reactions in DMF- $d_7$ and CD<sub>3</sub>CN as solvents. NMR Young tubes with the samples were heated at 100 °C and periodically monitored by <sup>1</sup>H NMR. Formation of a complex mixture of unidentified products was evident by <sup>1</sup>H NMR spectroscopy.

# Attempted reductive elimination from (dpms)Pt<sup>IV</sup>Ph(NHPh)(OH) (10)

#### Reaction in CD<sub>3</sub>CN

A sample of (dpms)PtPh(NHPh)(OH) (3 mg, 5  $\mu$ mol) and 0.7 mL of CD<sub>3</sub>CN were placed into an NMR Young tube and Teflon-sealed under argon. The reaction mixture was heated at 80 °C for 5 h; dark precipitate and dark-coloured solution formed. The only product present in the solution after 5 h was (dpms)PtPh(CD<sub>3</sub>CN), according to <sup>1</sup>H NMR spectroscopy and ESI-MS. Characteristics of the product are identical to those of (dpms)PtPh(CD<sub>3</sub>CN) obtained by dissolving (dpms)PtPh(MeOH) in CD<sub>3</sub>CN.

<sup>1</sup>H NMR (CD<sub>3</sub>CN, 22 °C)  $\delta$ : 5.82 (s, 1H), 6.92–7.03 (m, 4H), 7.24 (dd, J = 7.5, 1.5 Hz, <sup>3</sup> $J_{195PtH}$  = 45 Hz, 2H), 7.52 (ddd, J = 7.9, 5.5, 1.5 Hz, 1H), 7.74 (dd, J = 7.9, 1.5 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.97 (td, J = 7.9, 1.5 Hz, 1H), 8.07 (td, J = 7.9, 1.5 Hz, 1H), 8.15 (dd, J = 5.7, 1.5 Hz, <sup>3</sup> $J_{195PtH}$  = 63 Hz, 1H), 8.85 (dd, J = 5.5, 1.5 Hz, 1H). ESI of acidified solution diluted with methanol exhibited only one peak, m/z 566.1 (Calcd. for (dpms)<sup>195</sup>PtPh(CD<sub>3</sub>CN)H<sup>+</sup>, C<sub>19</sub>H<sub>15</sub>D<sub>3</sub>N<sub>3</sub>O<sub>3</sub><sup>195</sup>PtS: 566.1).

The precipitate formed in the reaction mixture was dissolved in DMSO- $d_6$ ; <sup>1</sup>H NMR spectrum of the resulting solution showed the presence of a complex mixture of unidentified products. No diphenylamine was detected by <sup>1</sup>H NMR.

#### Reaction in DMF-d<sub>7</sub>

Upon heating at 60 °C, the starting material slowly disappeared, and an insoluble product formed. After heating the sample at 80 °C for 24 h, complex mixture of product formed in DMF- $d_7$  solution and a dark precipitate.

#### X-ray structure determinations

The X-ray intensity data were measured at 220(2) K (0 K = 273.15 °C) on a three-circle diffractometer system equipped with Bruker Smart1000 CCD area detector using a graphite monochromator and a Mo K $\alpha$  fine-focus sealed tube ( $\lambda = 0.71073$  Å) operated at 50 kV and 40 mA. Details of the data collections and structure refinements are given in Table 1. Supplementary information for this article is available on the Web.<sup>4</sup>

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#### References

- (a) T. Punniyamurthy, S. Velusamy, and J. Iqbal. Chem. Rev. 105, 2329 (2005); (b) S.S. Stahl. Angew. Chem., Int. Ed. 43, 3400 (2004).
- A.N. Vedernikov, J.C. Fettinger, and F. Mohr. J. Am. Chem. Soc. 126, 11160 (2004).
- 3. A.N. Vedernikov, S.A. Binfield, P.Y. Zavalij, and J.R. Khusnutdinova. J. Am. Chem. Soc. **128**, 82 (2006).
- 4. J.R. Khusnutdinova, P.Y. Zavalij, and A.N. Vedernikov. Organometallics, **26**, 3466 (2007).
- 5. J.R. Khusnutdinova, P.Y. Zavalij, and A.N. Vedernikov. Organometallics, **26**, 2402 (2007).
- J.R. Khusnutdinova, L. Newman, P.Y. Zavalij, Y.-F. Lam, and A.N. Vedernikov. J. Am. Chem. Soc. 130, 2174 (2008).
- 7. A.E. Shilov and G.B. Shulpin. Chem. Rev. 97, 2879 (1997).
- 8. M. Lersch and M. Tilset. Chem. Rev. 105, 2471 (2005).
- 9. V.V. Rostovtsev, L.M. Henling, J.A. Labinger, and J.E. Bercaw. Inorg. Chem. 41, 3608 (2002).
- (a) J.P. Collman, L.S. Hegedus, J.R. Norton, and R.G Finke. Principles and applications of organotransition metal chemistry. University Science Books. Sausalito, CA. 1987; (b) B.J. Coe and S.J. Glenwright. Coord. Chem. Rev. 203, 5 (2000).
- K. Nakamoto. Infrared and raman spectra of inorganic and coordination compounds. Part II: Applications in coordination, organometallic, and bioinorganic chemistry. 5th Ed. Wiley. New York. 1997.
- M.B. Smith and J. March. March's advanced organic chemistry: reactions, mechanisms, and structure. 5th Ed. Wiley. New York. 2001.
- B.S. Williams, A.W. Holland, and K.I. Goldberg. J. Am. Chem. Soc. 121, 252 (1999).
- D.M. Crumpton-Bregel and K.I. Goldberg. J. Am. Chem. Soc. 125, 9442 (2003).
- G.A. Luinstra, J.A. Labinger, and J. E. Bercaw. J. Am. Chem. Soc. 115, 3004 (1993).
- B.S. Williams and K.I. Goldberg. J. Am. Chem. Soc. 123, 2576 (2001).
- A. Yahav-Levi, I. Goldberg, A. Vigalok, and A.N. Vedernikov. J. Am. Chem. Soc. 130, 724 (2008).
- R.G. Parr and W. Yang. Density functional theory of atoms and molecules. Oxford University Press. Oxford, UK. 1989.
- J.P. Perdew, K. Burke, and M. Ernzerhof. Phys. Rev. Lett. 77, 3865 (1996).
- (a) D.N. Laikov. Chem. Phys. Lett. 281, 151 (1997); (b) D.N. Laikov and Yu.A. Ustynyuk. Russ. Chem. Bull. 54, 820 (2005).
- (a) W.J. Stevens, H. Basch, and M. Krauss. J. Chem. Phys. 81, 6026 (1984); (b) W.J. Stevens, H. Basch, M. Krauss, and P. Jasien. Can. J. Chem. 70, 612 (1992); (c) T.R. Cundari and W.J. Stevens. J. Chem. Phys. 98, 5555 (1993).

<sup>&</sup>lt;sup>4</sup> Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3796. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/irm/unpub\_e.shtml. CCDC 683095 and 683096 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).