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Stoichiometric aerobic aminohydroxylation of ethylene mediated by dpms–platinum complexes (dmps = di(2-pyridyl)methanesulfonate)

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ABSTRACT

Chloro di(2-pyridyl)methanesulfonate ethylene platinum(II) complex was converted to corresponding N-alkylplatina(II)azetidines by reacting the former with primary amines, $MeNH_2$ and *tert*-$BuNH_2$, to produce 2-ammonioethyl chloro platinum(II) species and their subsequent cyclization in the presence of NaOH in methanol. The N-alkylplatina(II)azetidines are oxidized under air or the atmosphere of pure O_2 to the corresponding N-alkylplatina(IV)azetidines in water or in methanol solution in the presence of one equivalent of a strong acid under ambient pressure at 22 °C. The resulting N-alkylplatina(IV)-azetidines undergo C–O reductive elimination in acidic aqueous solutions to produce 2-(N-alkylamino)-ethanols.

1. Introduction

Selective 1,2-difunctionalization of alkenes such as 1,2-dihydroxylation and 1,2-aminohydroxylation is of great practical interest as a synthetic method for preparation of practically important and biologically relevant molecules [1,2]. A number of selective protocols for olefin aminooxygenation have been developed over the last few decades. These reactions are catalyzed by osmium [3], palladium [4–6], and platinum [7] complexes. However, most of the existing methods for catalytic aminooxygenation require the use of a strong oxidant such as iodobenzene diacetate [4,5] or N-chloroamines [3]. The only example of aerobic Pt-catalyzed 1,2-aminooxygenation of alkenes has recently been reported by Muniz et al. [7]. However, up to 30 mol.% copper(II) salts are utilized in this reaction to re-oxidize lower valent platinum species. One of the possible approaches toward developing selective *mediatorless* aminooxygenation of olefins using O_2 as the sole oxidant is the use of ligands that enable selective aerobic oxidation of the catalytic intermediates [8]. The requirement of overall high reaction selectivity translates into the requirement of high selectivity at each of the reaction steps, including the step of O_2 activation. From this perspective search for and study of selective reactions of organotransition metal complexes with O_2 is an important goal [8–10].

Previously we have reported that facially chelating di(2-pyridyl)methanesulfonate ligand, dpms, enables selective aerobic functionalization of aqua methyl platinum(II) complex (dpms)Pt^{II}-$Me(OH_2)$ and a series of platinum(II) hydroxo olefin complexes leading to MeOH, Me_2O [11,12], olefin oxides [13,14] and glycols [14], respectively (Scheme 1). In the two latter cases organic products with two new C–O bonds are formed. Overall, the reactions in Scheme 1 include formation of the corresponding platinum(IV) alkyls **1a**, **2**, **3** and the subsequent C–O reductive elimination from these platinum(IV) species.

In an effort to expand the scope of aerobic functionalization of olefins in (dpms)Pt-systems and explore the possibility of C–N/C–O olefin difunctionalization we studied transformations of the chloro ethylene complex (dpms)$Pt^{II}Cl(C_2H_4)$, **4** [14], in the presence of primary amines RNH_2, R = Me, *tert*-Bu, and dioxygen. In this work we report selective oxidative coupling of the ethylene ligand in **4** with RNH_2 with O_2 as oxidant to produce 2-(N-alkylamino)ethanol-derived salts **8a** and **8b** (Scheme 2). This transformation involves several steps. The first step includes facile external nucleophilic addition of RNH_2 to the ethylene ligand in **4** to form 2-ammonioethyl chloro platinum(II) complexes **5a**–**5b** (Scheme 2a). The latter can be readily converted to platina(II)azetidines (1,2-azaplatinacyclobutanes) **6a**–**6b** in the presence of bases (Scheme 2b). The azetidines **6a–6b** can be oxidized with O_2 to produce the corresponding platina(IV)azetidines **7a–7b** in high yield in acidic media (Scheme 2c). The subsequent C–O reductive elimination from the platina(IV)azetidines occurs in the presence of acids and leads to the products of C–N/C–O ethylene difunctionalization **8a–8b** (Scheme 2c).

Azametallacyclobutanes can be generated via a number of routes and have been proposed as intermediates in various

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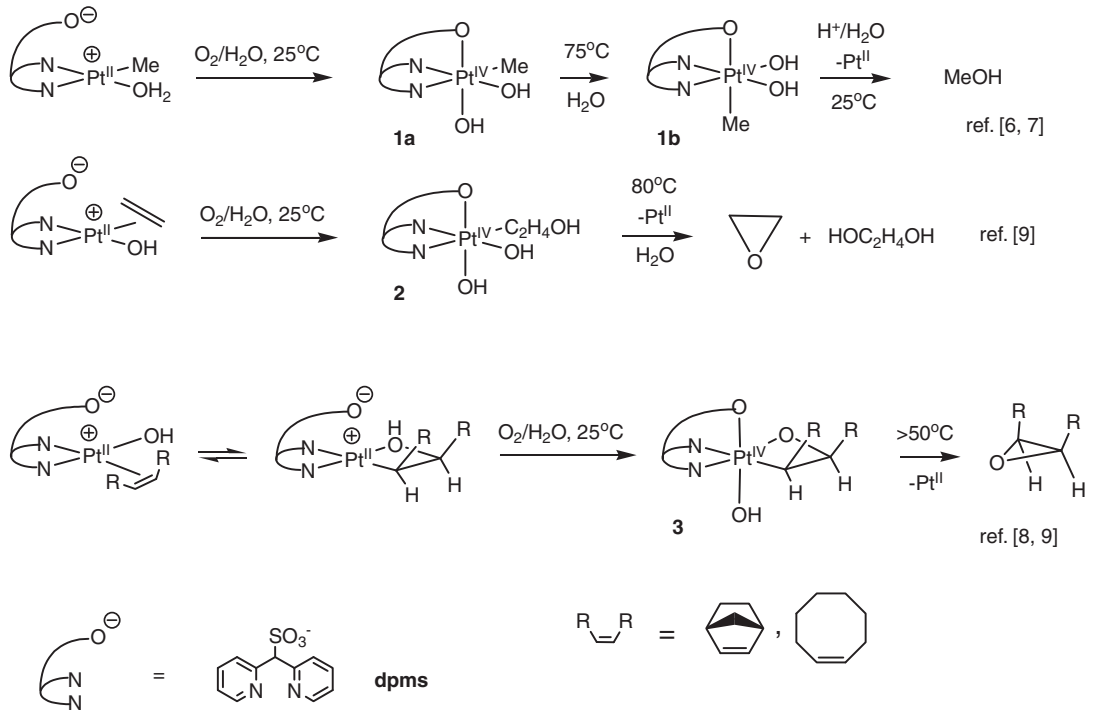
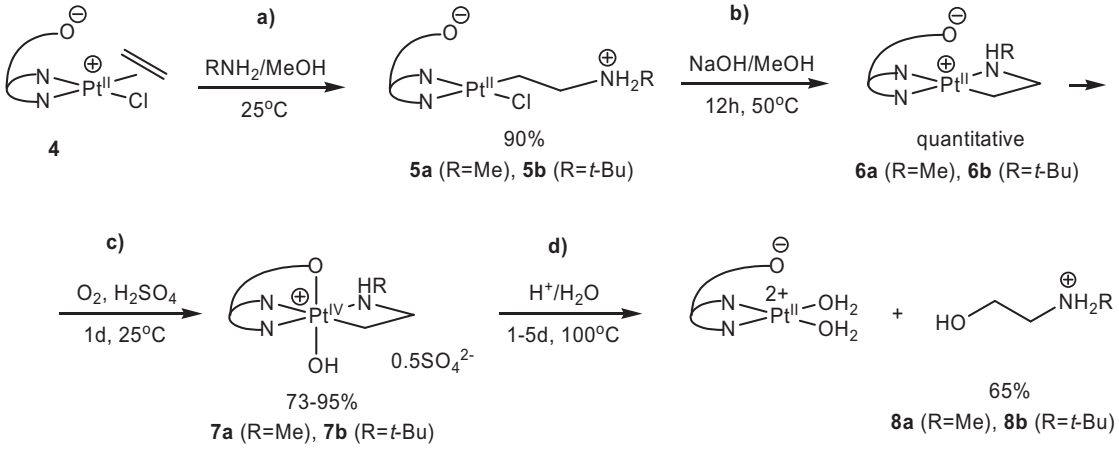


Scheme 1.



Scheme 2.

catalytic transformation such as alkene hydroamination [15] and aziridine isomerization or functionalization [16–18]. Apart from the external nucleophilic attack of an amine at the coordinated alkene, the most important routes leading to azametallacyclobutanes involve [2+2] cycloaddition of alkenes to metal imides [19,20], cyclometalation of amines first reported by Bergman [21,22], oxidative addition of aziridines, and intramolecular insertion of alkene into metal-amide bond [23,24]. The presented study of oxidative transformations of azaplatinacyclobutanes may be important for developing some alternative routes for metal-mediated functionalization of organic substrates.

2. Results and discussion

2.1. Synthesis of (dpms)$Pt^{II}Cl(C_2H_4NH_2R)$ complexes (R = Me, t-Bu) (dpms)$Pt^{II}Cl(C_2H_4NH_2Me)$, *5a*

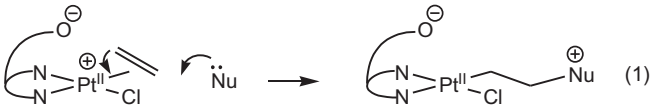
The zwitterionic 2-methylammonioethyl platinum(II) complex **5a** was prepared by reacting 5 equ of 40% aqueous solution of methylamine with a suspension of (dpms)$Pt(C_2H_4)Cl$, **4**, in methanol at room temperature (Scheme 2a). The product **5a** was isolated from the cold reaction mixture by filtration as an analytically pure white fine-crystalline solid in 90% yield. The complex is stable under air both in the solid state and in aqueous or methanolic solutions but decomposes slowly in DMSO to produce ethylene gas among other products. Complex **5a** has been characterized by ^1H, ^{13}C NMR spectroscopy as well as by electro-spray ionization mass spectrometry (ESI-MS). The ESI-MS spectra of aqueous or methanolic solutions of **5a** show the presence of **5a**·H^+ ion as the only Pt-containing species. Both ^1H and ^{13}C NMR spectra contain a full set of signals corresponding to two non-equivalent pyridyl fragments, consistent with low symmetry of **5a**. Accordingly, two pairs of diastereotopic hydrogen atoms present in the ethylene residue produce four signals in the range of 1.21–3.04 ppm, two of which are accompanied by discernible platinum-195 satellites with the coupling constant $^2J_{PtH}$ of 72 and 52 Hz. The ethylene proton resonances are shifted upfield as compared to the ethylene ligand signals in

the complex **4**, 4.9 and 5.1 ppm. ^{1}H NMR spectra of **5a** in DMSO solutions show a broad singlet at 8.29 ppm integrating as 2H, consistent with the presence of an ammonium fragment in **5a**.

2.2. (dpms)Pt^{II}Cl($C_2H_4NH_2$t-Bu), **5b**

The *tert*-butyl analog **5b** was prepared in a similar fashion as **5a** by adding 5 equ of *tert*-butylamine to a suspension of complex **4** in methanol. The mixture produced a clear solution after few minutes. Subsequent crystallization overnight at −20 °C led to the formation of large white crystals of **5b** which were separated from the cold mixture. The yield of an analytically pure product is 89%. The air-stable complex **5b** has been characterized by ^{1}H, ^{13}C NMR spectroscopy as well as by ESI-MS and showed the expected spectral patterns similar to those observed for **5a**.

Overall, transformation of **4**–**5a** or **5b** presented in Scheme 2a can be viewed as a result of an outer-sphere attack of nucleophilic nitrogen atom of an amine RNH_2 at one of the carbon atoms of the coordinated ethylene:



(1)

This transformation is similar to the chemistry observed for **4** in aqueous alkaline solutions involving nucleophilic attack of hydroxide at the coordinated ethylene resulting in an anionic 2-hydroxoethyl chloro platinum(II) complex (dpms)Pt^{II}Cl(C_2H_4OH)$^-$ [14].

2.3. Formation of platina(II)azetidine complexes **6a**–**6b**, (dpms)Pt^{II}(C_2H_4NHR-κC,κN), R = Me, t-Bu

Cyclization of 2-N-alkylaminoethyl chloro platinum(II) complexes **5a–5b** to platina(II)azetidines **6a–6b** could be achieved in the presence of methanolic solution of NaOH at 50 °C (Scheme 2b). These complexes were characterized by means of ^{1}H and ^{13}C NMR spectroscopy and ESI-MS and could be used without further purification to prepare platina(IV)azetidines **7a–7b**.

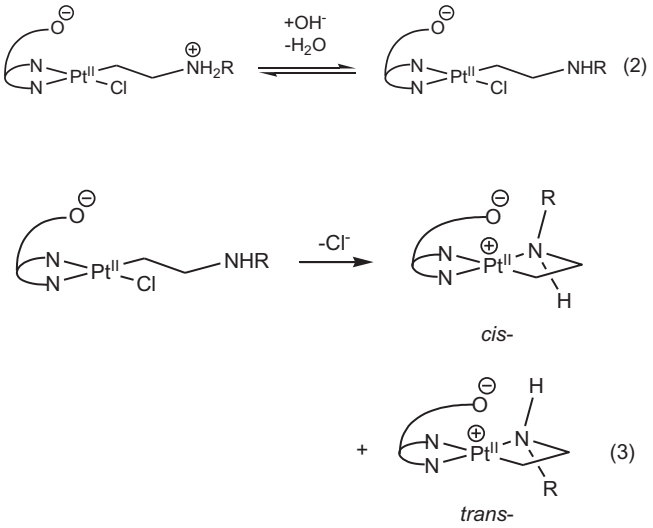
2.4. (dpms)Pt^{II}(C_2H_4NHMe-κC,κN), **6a**

White solid produced from **5a** and two equivalents of NaOH could be separated from the mixture after 24 h by filtration and washing with water to remove water-soluble inorganic compounds in 76% yield. The reaction is not complete if stoichiometric amount of NaOH is used. The product was used to prepare corresponding platina(IV)azetidine **7a** without further purification. Poor solubility of **6a** in common solvents prevented from obtaining good quality ^{1}H and ^{13}C NMR spectra for this compound. ESI-MS spectra of dilute solutions of **5a** in aqueous methanol showed the presence of the cation **6a**·H$^+$.

2.5. (dpms)Pt^{II}($C_2H_4NH_2$t-Bu-κC,κN), **6b**

Heating a stirred suspension of **5b** in methanol with 1 equ of NaOH at 50 °C leads to dissolution of the starting material after ~30 min. According to ^{1}H NMR spectroscopy, no starting material was present in the reaction mixture after 12 h. The product **6b** was identified by ESI-MS in the form of the cation **6b**·H$^+$. Two sets of signals assigned to two isomers of **6b** present in 6:1 ratio were observed in its ^{1}H NMR spectra. Two isomeric azetidines **6b** may differ by the configuration of the nitrogen atom of the azetidine ring.

Formation of the azetidines **6a–6b** can be viewed as a result of an intramolecular ligand substitution at the Pt^{II} center with the chloro ligand as the leaving group and the nitrogen atom of the 2-aminoethyl ligand as the nucleophile. An alkali metal hydroxide additive is required to deprotonate the ammonium group present in **5a–5b** and generate the required nucleophile, Eqs. (2) and (3):



2.6. Attempted aerobic oxidation of platina(II)azetidines **6a**–**6b** in methanol in the absence and in the presence of NaOH

Our previous study of aerobic oxidation of (dpms)Pt^{II}R(HX) complexes where R = Me, Ph and HX = H_2O [11,12,14], MeOH [12,25] or $PhNH_2$, $MeNH_2$ [25] led us to the hypothesis that the actual species responsible for dioxygen activation are the corresponding anionic complexes (dpms)Pt^{II}Me(X)$^-$ resulting from deprotonation of the coordinated HX ligand [14,25]. Accordingly, in the case of the relatively acidic ligands HX such as H_2O and MeOH the presence of a base additive is beneficial for faster oxidation kinetics of (dpms)Pt^{II}R(HX) complexes.

To test the effect of base additives on the reactivity of **6b** towards O_2 a solution of **6b** in methanol was combined with 0.2 equ of NaOH and stirred under oxygen atmosphere at 22 °C. According to NMR spectroscopy, the starting material remained unchanged after 4 days. Similarly, no changes were observed, according to NMR spectroscopy, in methanolic solution of **6b** which contained no additives and was stirred under O_2 atmosphere for 2 days at 22 °C. It is therefore reasonable to assume that the acidity of the NH group of azetidine **6b** is not high enough to allow for its deprotonation with NaOH in a sufficient extent.

2.7. Aerobic oxidation of platina(II)azetidines **6a**–**6b** to platina(IV)azetidines **7a**–**7b** (R = Me, t-Bu) in the presence of acid additives

Interestingly, in contrast to base additives, one equivalent HBF_4 or H_2SO_4 enables aerobic oxidation of platina(II)azetidines to their platina(IV)azetidine analogs **7a** and **7b** (Scheme 2c).

Solutions of complexes **6a** and **6b** in methanol or water containing one equivalent of a strong acid react under O_2 at 22 °C to produce the platina(IV)azetidines **7a** and **7b** in 93% and 73% NMR yield, respectively as the main product. The identity of **7a** and **7b** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, ESI mass spectrometry and, in the case of **7b**, single crystal X-ray diffraction. Oxidation of **6a** in the aqueous solution was complete after 2 h under

O_2 atmosphere, whereas a slower reaction was observed under air with a half life of *ca.* 2 h. The reaction is complete after 24 h to give **7a** in 92% yield. Besides **7a** and **7b** some unidentified products formed in 5–27% yield. Complexes **7a** and **7b** can be prepared more conveniently if the oxidation of **6a** and **6b** is performed with hydrogen peroxide (*vide infra*).

The surprising effect of acid additives on the reactivity of platina(II)azetidines **6a–6b** is opposite to what was observed for other (dpms)Pt^{II}R(HX) complexes [8]. This effect can be accounted for assuming an acid-promoted reversible conversion of these platina(II)azetidines to the corresponding solvento 2-ammonioethyl complexes **A** (Scheme 3a, HX = H_2O or MeOH) that react further with O_2 to form the corresponding acyclic 2-ammonioethyl platinum(IV) complexes **B** (Scheme 3b), according to the mechanism assumed previously for (dpms)Pt^{II}R(HX) complexes [25]. We presume that complexes **B** can subsequently cyclize to form the azetidines **7a–7b** (Scheme 3c). The latter reaction may be less efficient compared to the oxidation step itself so accounting for less than quantitative yield of the platinum(IV) products, which is observed normally in aerobic oxidation of (dpms)Pt^{II}R(HX) complexes. A reversible transformation of acyclic 2-ammonioethyl chloroplatinum(IV) complexes into the corresponding platina(IV)azetidines was observed earlier [26].

2.8. Oxidation of platina(II)azetidines **6a–6b** to platina(IV)azetidines 7a–7b with hydrogen peroxide (R = Me, t-Bu)

The use of a stronger oxidant, hydrogen peroxide, allows for faster reaction rates and therefore for a more convenient preparation of complexes **7a–7b**.

2.8.1. (dpms)Pt^{IV}(OH)(C_2H_4NHMe-κC,κN)$^+$, **7a**

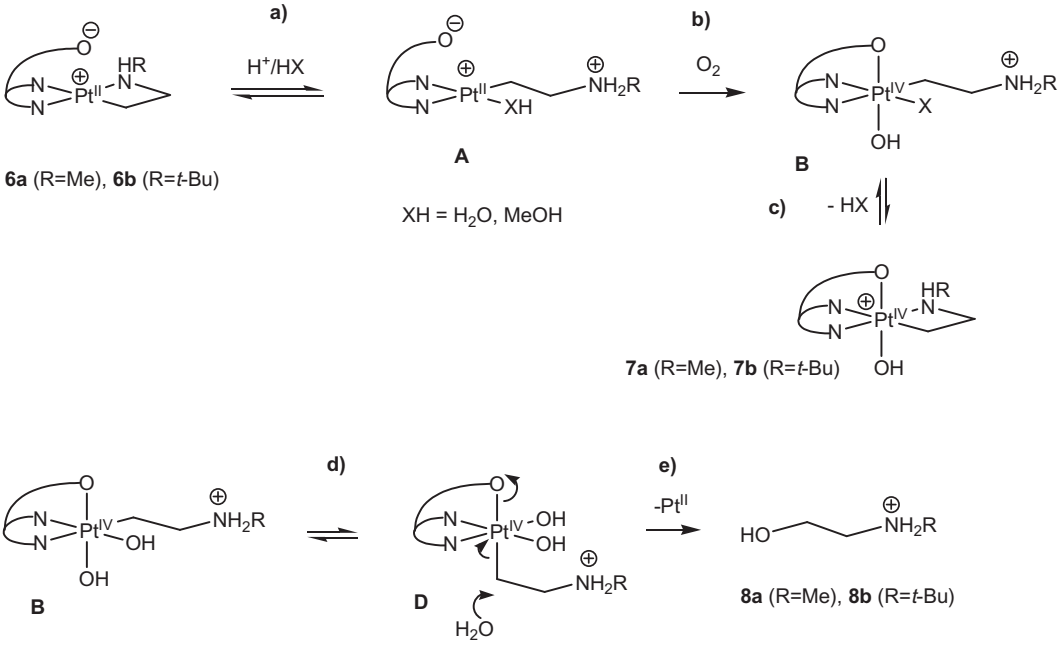
Complex **6a** suspended in methanol reacts with 1.1 equ 30% aqueous H_2O_2 at 22 °C to produce in a few minutes a yellow strongly alkaline solution containing **7a**. According to ^{1}H NMR spectroscopy, formation of **7a** is quantitative after 1 h. The product forms as a mixture of two isomers in 2:1 ratio, presumably with different configuration at the azetidine nitrogen atom, *cis*- and *trans*-, similar to **6b**. Importantly, this ratio is 2:5 after 1 h upon completion of the oxidation but it grows to 2:1 after 10 h and remains further unchanged. The resulting alkaline solution of **7a**(OH) was neutralized with one equivalent H_2SO_4, evaporated to dryness to produce white crystalline [(dpms)Pt^{IV}(C_2H_4NMe-κC,κN)(OH)]$_2$(SO_4) quantitatively. The resulting samples of solid (**7a**)$_2$(SO_4) decompose slowly at room temperature.

The product was characterized by ESI-MS, ^{1}H, ^{13}C, COSY and HSQC NMR spectroscopy. The ^{1}H NMR spectrum of **7a** in methanol exhibits two sets of signals, one for the major and one for the minor isomer, each including signals of two non-equivalent pyridyl fragments of the dpms ligand, four multiplets for the ethylene residue in the range of 2.8–4.5 ppm, two of which have discernible platinum-195 satellites with the coupling constant $^2J_{PtH}$ of 79 Hz, and the signal of the methyl group at the azetidine nitrogen with platinum-195 satellites and the coupling constant $^3J_{PtH}$ of 33 Hz. The latter feature suggests a metallacyclic structure for both isomers of **7a**.

In ^{13}C NMR spectra of the major isomer of **7a**, signals of the azetidine ring carbon atoms appeared at −2.0 ppm ($^1J_{PtC}$ = 414 Hz) and 80.3 ppm ($^2J_{PtC}$ = 115 Hz), which were assigned to the Pt-bound and N-bound carbon atoms, respectively. The signal of N–Me group was observed at 56.0 ppm and was accompanied by platinum satellites ($^2J_{PtC}$ = 22 Hz).

2.8.2. (dpms)Pt^{IV}(OH)(C_2H_4NHt-Bu-κC,κN)$^+$, **7b**

A solution of complex **6b** prepared from **5b** and one equivalent NaOH in MeOH was used to synthesize (**7b**)Cl. Upon addition of 11 equ of 30% aqueous H_2O_2 to this solution the reaction mixture turned yellow. According to ^{1}H NMR spectroscopy, formation of **7b** is quantitative after 30 min. The product (**7b**)Cl can be isolated from the mixture upon its concentration and crystallization at −20 °C. The isolated yield of an analytically pure (**7b**)Cl is 64%. The product is a white crystalline solid perfectly soluble in methanol, water and DMSO, slightly soluble in THF. From methanol (**7b**)Cl crystallizes with one molecule of the solvent which could not be removed even after drying under high vacuum (50 mTorr) for several days. The methanol solvate was fully characterized including ^{1}H and ^{13}C NMR spectroscopy, ESI-MS, elemental analysis and single crystal X-ray diffraction



Scheme 3.

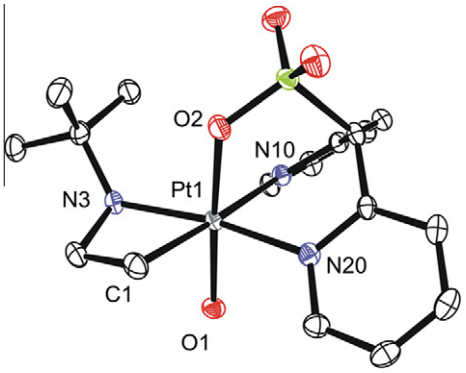


Fig. 1. ORTEP drawing for the cation (dpms)Pt^{IV}(κ^2-*N*,*C*-C_2H_4N–*t*-Bu)OH]$^+$, **7b**, (50% probability ellipsoids); hydrogen atoms are omitted for clarity. Selected bond lengths, Å, and angles, °: Pt1–C1, 2.039(3); Pt1–O1, 1.970(2); Pt1–O2, 2.066(2); Pt1–N3, 2.072(3); Pt1–N10, 2.195(3); Pt1–N20, 2.053(3); Pt1–C1–C2, 94.0(2); C1–C2–N3, 100.6(3); C2–N3–Pt1, 92.7(2); C1–Pt1–N3, 69.39(13).

(Fig. 1). According to the X-ray diffraction data, chloride counterion is hydrogen-bound to both NH and OH fragments present in the cation **7b**.

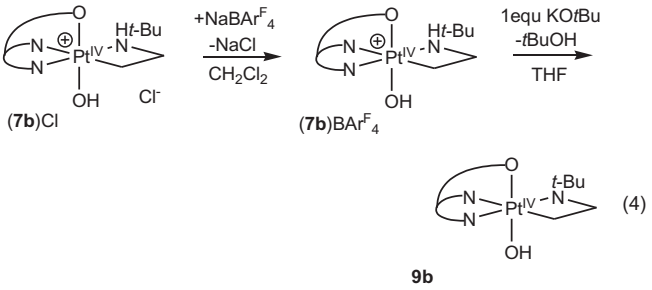
The NMR spectral pattern observed for **7b** in methanol is similar to that observed for its methyl analog **7a** with one notable difference: in contrast to **7a**, one set of signals was observed in ^{1}H NMR spectra of **7b**. Based on the X-ray diffraction data, we tentatively assign the configuration of **7b** present in solutions also as *cis*-, which may be expected to be more favorable due to a weaker steric repulsion between the *tert*-Bu group and the *ortho*-pyridyl hydrogen atoms in *cis*-**7b**.

Notably, ^{1}H NMR spectra of **7b** in DMSO showed also the presence of two broad singlets at 4.25 ppm and 7.60 ppm that were assigned to the protons of the Pt–OH and Pt–NH fragments, respectively. The latter signal has discernible platinum satellites with the coupling constant $^2J_{PtH}$ of 58 Hz. Two multiplets of the platinum-bound ethylene α-CH_2 group accompanied by platinum satellites are centered at 2.89 ppm, $^2J_{PtH}$ = 75 Hz, and 2.94 ppm, $^2J_{PtH}$ = 70 Hz. The multiplets of the N-bound β-CH_2 group have platinum-195 satellites as well and are centered at 4.41 ppm, $^3J_{PtH}$ = 35 Hz, and 4.58 ppm, $^3J_{PtH}$ = 40 Hz, each integrating as one proton relative to the signal of the *tert*-butyl group whose signal intensity was assigned to 9H.

The ^{13}C NMR spectra of **7b** exhibited two resonances of the carbon atoms of the azetidine ring at −4.1 ppm (Pt-bound) and 54.3 ppm (N-bound). The signals are characterized by ^{195}Pt–C coupling constants of 376 Hz and 114 Hz, respectively. Notably, complex (**7b**)Cl represents the first example of the structurally characterized platina(IV)azetidine [26].

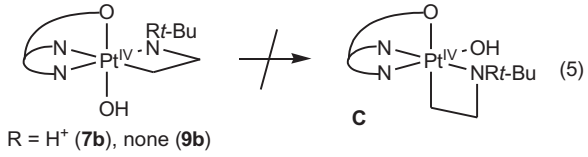
2.9. Attempted C–N reductive elimination from **7b** in THF, benzene and DCM solutions

One can expect a similar C–X reductive elimination reactivity for structurally similar platina(IV)oxetanes **3** and platina(IV)azetidines **7a–7b**, X = O or N. Holding this consideration in mind we attempted C–N reductive elimination from **7a–7b** in the absence and presence of a base, KO*t*-Bu, using aprotic solvents, THF, benzene and dichloromethane. In all the cases decomposition of the starting material was observed. For instance, (**7b**)[tetrakis(3,5-bis(trifluoromethyl)phenyl)borate], (**7b**)$BArF_4$, prepared by metathesis of (**7b**)Cl and $NaBArF_4$ in dry dichloromethane was deprotonated upon addition of 1 equ KO*t*-Bu in THF and removal of the resulting *tert*-butanol under vacuum to produce a mixture of $KBAr^F{}_4$ and the neutral azetidine **9b**, Eq. (4):



The resulting mixture containing azetidine **9b** was characterized by ^{1}H NMR spectroscopy in THF-d_8 solutions. The most prominent difference between ^{1}H NMR characteristics of (**7b**)BAr^F and **9b** is the absence of the NH group signal at 5.9 ppm, whereas the OH group singlet was only slightly shifted upfield to 3.23 ppm as compared to from 3.43 ppm for **7b**. Upon dissolution of this mixture in THF-d_8 and heating at 60 °C decomposition was observed with a half-life of 22 h to form some unidentified insoluble products. Upon completion of the reaction after 4 days the resulting solid was dissolved in DMSO and analyzed by means of ESI-MS and NMR spectroscopy. No free aziridine or its platinum(II) complex, the expected C–N reductive elimination products, were detected.

One of the possible reasons for the lack of reactivity of **7b** and **9b** in C–N reductive elimination might be very slow transformation of these azetidines into isomer **C** featuring the alkyl group *trans*- to the sulfonate, Eq. (5). Presumably, the slow isomerization cannot compete with some side reactions which lead to decomposition of the azetidine.



Similar lack of isomerization reactivity in aprotic organic solvents was also observed previously for (dpms)Pt^{IV}R(HNPh)(OH), R = Me, Ph [25]. At the same time, it has been established that (dpms)Pt^{IV}R complexes with the hydrocarbyl R *trans*- to the sulfonate leaving group, such as **1b** in Scheme 2, are responsible for the C–O reductive elimination reactivity [11–14].

2.10. Reductive elimination of *N*-alkylethanolamines **8a–8b** from platina(IV)azetidines **7a–7b** in acidic aqueous solutions

Attempted reductive elimination of *N*-methyl substituted platina(IV)azetidine **7a** in alkaline and neutral aqueous solutions at 100 °C produced a complex mixture of products. No *N*-methyl ethanolamine was detected among the reaction products in alkaline solutions of **7a**, but some trace amount (<5%) of *N*-methyl ethanolamine was detected in neutral solutions of **7a**(BF_4) after heating it at 100 °C for 3 days, according to ^{1}H NMR spectroscopy.

Importantly, in the presence of one equivalent of HBF_4 or H_2SO_4, clean formation of the corresponding of 2-(*N*-alkylamino)ethanols in the form of ammonium salts **8a–8b** occurred with a half-life of about 3 h at 100 °C (Scheme 2d). These products were identified by ^{1}H NMR spectroscopy and ESI-MS by comparison with authentic samples. The NMR yield of **8a** and **8b** is 63–65% after 30 h of reaction. The main platinum-containing products identified by means of ^{1}H NMR spectroscopy are (dpms)$Pt^{II}(OH_2)_2^+$ and water-insoluble

$(dpms)_2Pt^{II}_2(\mu\text{-}OH)_2$ which dissolves in water in the presence of excess HBF_4 [11].

The ability of platina(IV)azetidines to undergo the acid-assisted C–O reductive elimination in water can be accounted for by assuming an initial azetidine ring opening to form dihydroxo alkyl platinum(IV) species **B** (Scheme 3c, X = OH). The resulting acyclic alkyl species might isomerize into **D** featuring the 2-ammonioalkyl *trans*- to the sulfonate group (Scheme 3d). This isomerization step is presumed to be much slower for the platina(IV)azetidines **7a–7b** rendering them unreactive in C–N reductive elimination. The isomer **D** can be attacked by nucleophilic water molecules to form the organic products **8a–8b**, following the nucleophilic substitution mechanisms discussed previously for **1a** [11,12] and **2** [14]. To gain evidence in favor of the proposed mechanism for the formation of **8a–8b**, the reaction mixtures containing **7a** and one equivalent of HBF_4 in water at 100 °C were monitored using ^1H NMR spectroscopy. A new species was detected in the course of the reaction whose fraction never exceeded 20% of the initial concentration of **7a**. Signals of the observed intermediate grew in the initial period of reaction, reached the maximum at about 6 h and disappeared after 30 h. This species was characterized by the multiplets at 3.86–4.06 ppm and a singlet at 2.48 ppm, integrating as 2H and 3H, respectively, which could be assigned to the resonances of the N-bound β-CH_2 group, and the N–Me group, respectively. The absence of platinum-195 satellites for the signal of the N–Me group at 2.48 ppm argues against the coordination of the N–Me group to the Pt center in the observed intermediate, consistent with the structure proposed for **B** (Scheme 3). Two matching peaks of the *ortho*-protons of the pyridyl groups of the dpms ligand were observed in the aromatic region as well, indicative of the low C_1 symmetry of the observed intermediate. Therefore, ^1H NMR characteristics of the observed species are consistent with those expected for **B** and not **D**. In contrast to **B**, the latter is expected to be very reactive in S_N2-type C–O reductive elimination [11,12,14]. Finally, according to ESI-MS, a new signal appeared and grew in aqueous solutions of **7a** containing H_2SO_4 during its heating. The peak is characterized by *m*/*z* 537.1 which matches the value expected for an acyclic species $[(dpms)Pt^{IV}(CH_2CH_2\text{-}NH_2Me)(OH)_2]^+$.

No β-hydride elimination or hydroamination products which are typically observed for platina(II)azetidines [15] have been detected in acidic solutions of the platina(IV)azetidines **7a** or **7b** upon heating. Thus, formation of high-valent platina(IV)azetidine complexes leads to preferential 1,2-difunctionalization of olefins in contrast to "monofunctionalization" observed for hydroamination or "aza-Wacker-process" mediated by Pt^{II} and Pd^{II} species [15,27]. Further investigation of aminohydroxylation of the substituted alkenes is required to elucidate the mechanism of the C–O reductive elimination from platina(IV)azetidines **7a–7b**.

3. Summary and conclusions

Overall, a mediatorless aerobic coupling of an ethylene chloro platinum(II) complex and primary alkylamines enabled by di(2-pyridyl)methanesulfonate ligand to form 2-(N-alkylamino) ethanols has been demonstrated in protic media. This multistep reaction includes nucleophilic attack of an amine at the ethylene chloro platinum(II) complex and subsequent cyclization of the resulting 2-ammonioethyl platinum(II) intermediates in basic media to form platina(II)azetidines. An important finding of this work is the discovery of the ability of platina(II)azetidines supported by di(2-pyridyl)methanesulfonate ligand to react with O_2 in acidic aqueous solutions at ambient temperature and pressure. The corresponding platina(IV)azetidines can be prepared in high yield. Interestingly, the presence of a strong acid additive is critical for the success of this transformation. The acid is presumed to promote the azetidine ring opening to produce an aqua 2-ammonioethyl platinum(II) intermediate which is expected to be reactive towards O_2, similar to other $(dpms)Pt^{II}R(OH_2)$ complexes studied previously. All attempts at direct C–N reductive elimination of aziridines from the platina(IV)azetidines in either aprotic or protic solvents were unsuccessful presumably because of unavailability of the isomer required for facile C–X reductive elimination. The final step of the platinum-mediated aerobic oxidative coupling of ethylene and a primary amine to 2-(N-alkylamino)ethanols is the C–O reductive elimination of platina(IV)azetidines that also requires the presence of one equivalent of a strong acid in aqueous solution. This reaction, most likely, includes acyclic 2-ammonioethyl platinum(IV) intermediates resulting from the azetidine ring opening and protonation of the basic amino group. Overall, the current work may be useful for mechanistic analysis and development of new systems for aerobic platinum-catalyzed aminooxygenation of olefins.

4. Experimental section

General. All manipulations were carried out under purified argon atmosphere using standard Schlenk and glove box techniques if not indicated otherwise. All reagents for which synthesis is not given are commercially available from Aldrich, Acros, Alfa-Aesar or Pressure Chemicals and were used as received without further purification. Potassium di(2-pyridyl)methanesulfonate and complex **4**, $(dpms)Pt(CH_2{=}CH_2)Cl$, were synthesizes as described previously [14,28]. DMSO-d_6, CD_2Cl_2 and CD_3OD from Cambridge Isotope Laboratories were dried over CaH_2, vacuum-transferred and stored in Teflon-sealed flasks in an argon-filled glove box. Water was deaerated by repeating freezing–pumping cycles and stored under argon in a Teflon-sealed Schlenk flask in a glove box. ^1H (400 MHz, 500 MHz or 600 MHz) and ^{13}C NMR (100 MHz or 125 MHz) spectra were recorded on a Bruker AVANCE 400, Bruker DRX-500 or Bruker AVANCE-600 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. GC–MS experiments were performed using a JEOL JMS-SX 102A instrument. Elemental analyses were carried out by Chemisar Laboratories, Inc., Guelph, Canada.

4.1. Preparation of $(dpms)Pt^{II}(C_2H_4NH_2Me)Cl$, **5a**

To a stirred suspension of $(dpms)Pt(C_2H_4)Cl$ (98 mg, 193 μmol) in 26 mL MeOH was added 40% aqueous solution of $MeNH_2$ (85 μL, 973 μmol, 5 equ). Stirring continued for 3 h at room temperature. The resulting suspension was left at −20 °C for 4 h. White fine-crystalline solid was filtered off from the cold mixture, washed with cold methanol and dried under vacuum to give 68.9 mg of the product. The volume of the filtrate was reduced to 1 mL, the resulting suspension was cooled down to −20 °C, filtered. The solid was washed with cold methanol to give an additional 24.7 mg of the product. Combined yield of **5a** is 93.6 mg (174 μmol), 90%. White crystalline solid, air-stable, poorly soluble in water and methanol, soluble in DMSO. Solutions of **5a** in dmso-d_6 decompose with a half-life of ~7 h at 20 °C to produce (dpms)PtCl(dmso-d_6), free ethylene (a singlet at 5.29 ppm) along with unidentified products.

^1H NMR (dmso-d_6, 22 °C, 400 MHz), δ: 1.02–1.41 (m, $^2J_{PtH}$ = 62 Hz, 1H), 2.10–2.41 (m, 2H), 2.33 (s, 3H), 2.59–2.84 (m, $^3J_{PtH}$ = 40 Hz, 1H), 6.00 (s, 1H), 7.41 (ddd, *J* = 7.8, 6.0, 1.5 Hz, 1H), 7.51 (ddd, *J* = 7.8, 5.6, 1.5 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.06 (td, *J* = 7.8, 1.5 Hz, 1H), 8.12 (td, *J* = 7.8,

1.5 Hz, 1H), 8.29 (br s, 2H, NH_2), 8.87 (d, J = 6.0 Hz, 1H), 9.03 (dd, J = 5.6, 1.5 Hz, 1H). **^{13}C NMR** (dmso-d_6, 22 °C, 500 MHz), δ: −0.7 (Pt–CH_2), 31.6 (N–CH_3), 53.6 (N–CH_2), 75.9 ($CHSO_3$), 124.1, 125.6, 128.0, 129.6, 137.9, 138.1, 150.5 (CH, py), 150.8 (C quat, py), 151.8 (CH, py), 154.0 (C quat, py) (signal assignments are from DEPT). IR (KBr), ν: 3468 (w br), 3135 (w), 3014 (w), 2945 (w), 2907 (w), 1601 (w), 1478 (w), 1433 (w), 1407 (w), 1314 (w), 1240 (s), 1170 (s), 1034 (s), 902 (w), 860 (w), 805 (w), 758 (s) cm^{-1}. ESI-MS of solution of **5a** in MeOH/H_2O (50:50 v/v): m/z 539.0; calc. M·H$^+$ $C_{14}H_{19}N_3SO_3{}^{195}Pt^{35}Cl$ 539.0. *Anal.* Calc. for $C_{14}H_{18}ClN_3O_3PtS$: C, 31.20; H, 3.37; N, 7.80. Found: C, 30.98; H, 3.63; N, 7.58%.

Complex (dpms)PtCl(dmso-d_6) was obtained independently by dissolving LPt(CH_2=CH_2)Cl in dmso-d_6. ^{1}H NMR of (dpms)PtCl(dmso-d_6) (dmso-d_6, 22 °C, 400 MHz), δ: 6.28 (s, 1H), 7.54 (ddd, J = 7.9, 5.9, 1.5 Hz, 1H), 7.64 (ddd, J = 7.9, 5.9, 1.5 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 8.18 (td, J = 7.9, 1.5 Hz, 1H), 8.22 (td, J = 7.9, 1.5 Hz, 1H), 8.83 (dd, J = 5.9, 1.5 Hz, 1H), 9.06 (dd, J = 5.9, 1.5 Hz, 1H).

4.2. Preparation of (dpms)Pt^{II}($C_2H_4NH_2$t-Bu)Cl, **5b**

A 100 mL round-bottom flask was charged with (dpms)Pt(C_2H_4)Cl (151 mg, 297 μmol) and 40 mL of methanol. *Tert*-butylamine (150 μL, 1.42 mmol, 5 equ) was added dropwise to the stirred suspension at room temperature. After a few minutes all starting material dissolved. Stirring continued for 1 h, and the resulting solution was left to crystallize overnight at −20 °C. White large crystals of the product were filtered off from the cold mixture, washed with several milliliters of cold methanol and dried under vacuum to give 115.7 mg of the product. An additional fraction of the product was obtained by reducing volume of the filtrate to 5 mL under vacuum. The resulting suspension was cooled down to −20 °C and filtered. The resulting solid was washed with 1 mL of cold methanol and vacuum-dried to give 38.4 mg of the pure product. Combined yield of **5b** is 154.1 mg (265 μmol), 89%. White crystalline solid, air-stable, poorly soluble in water in methanol; soluble in DMSO.

^{1}H NMR ^{1}H (dmso-d_6, 22 °C, 400 MHz), δ: 0.91–1.23 (m, 1H, $^2J_{PtH}$ could not be determined), 1.18 (s, 9H), 2.16–2.49 (m, 2H), 2.92–3.13 (m, $^2J_{PtH}$ = 50 Hz, 1H), 5.95 (s, 1H), 7.41 (ddd, J = 7.8, 5.7, 1.5 Hz, 1H), 7.50 (ddd, J = 7.8, 5.5, 1.3 Hz, 1H), 7.77 (d, J = 7.8, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.92 (br s, 2H, NH_2), 8.05 (td, J = 7.8, 1.7 Hz, 1H), 8.09 (td, J = 7.8, 1.5 Hz, 1H), 8.71 (d, J = 5.7 Hz, 1H), 9.05 (dd, J = 5.5, 1.3 Hz, 1H). **^{13}C** NMR (dmso-d_6, 22 °C, 500 MHz), δ: −0.77 ($^1J_{PtC}$ = 760 Hz), 25.33, 45.87, 55.34, 75.74, 124.15, 125.55, 128.22, 129.49, 137.75, 138.05, 150.46, 151.03, 152.46, 154.01. IR (KBr), ν: 3474 (w br), 3414 (w br), 3057 (w), 2974 (w), 2835 (w), 1604 (w), 1476 (w), 1457 (w), 1430 (w), 1376 (w), 1304 (w), 1247 (m), 1236 (m), 1211 (s), 1178 (s), 1159 (m), 1039 (s), 854 (w), 808 (w), 763 (m) cm^{-1}. ESI-MS for solution of **5b** in MeOH/H_2O (50:50 v/v), m/z 581.1, calc. M·H$^+$, $C_{17}H_{25}N_3SO_3{}^{195}Pt^{35}Cl$ 581.1. *Anal.* Calc. for $C_{17}H_{24}ClN_3O_3PtS$: C, 35.14; H, 4.16; N, 7.23. Found: C, 34.84; H, 4.28; N, 6.86%.

Complex **5b** decomposes in dmso-d_6 solutions at 20 °C with a half-life of 22 h to produce (dpms)PtCl(dmso-d_6), ethylene (a singlet at 5.29 ppm) and unidentified products.

4.3. Preparation of (dpms)Pt^{II}(C_2H_4NHMe-κC,κN), **6a**

A 100 mL Schlenk tube equipped with a magnetic stirring bar was charged with 91.2 mg of **5a** (169 μmol) and 18 mL of 18.8 mM NaOH solution in degassed MeOH (338 μmol, 2 equ NaOH). The Schlenk tube was Teflon-sealed under argon and heated at 50 °C for 24 h. The resulting suspension was cooled down to room temperature and the white precipitate was filtered off, washed with methanol until a neutral pH of the filtrate and dried under vacuum to give 56.0 mg of **6a**. Volume of the filtrate was reduced to 2 mL under vacuum and the crude product was filtered off, washed with cold methanol and dried to give 8.8 mg of **6a**. Yield 64.8 mg (129 μmol), 76%. White crystalline solid, poorly soluble in methanol.

^{1}H NMR (dmso-d_6, 22 °C, 400 MHz), δ: 0.98–1.12 (m, $^2J_{PtH}$ = 60 Hz, 1H), 1.18–1.34 (m, $^2J_{PtH}$ = 55 Hz, 1H), 2.30 (d, J = 5.5 Hz, $^3J_{PtH}$ ~ 20 Hz, 3H), 4.03–4.24 (m, $^3J_{PtH}$ ~ 50 Hz, 1H), 4.97–5.33 (m, 2H), 5.81 (s, 1H), 7.30 (ddd, J = 7.7, 5.6, 1.5 Hz, 1H), 7.53 (ddd, J = 7.7, 5.6, 1.5 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 7.7 Hz, 1H), 8.05 (td, J = 7.7, 1.5 Hz, 1H), 8.09 (td, J = 7.7, 1.5 Hz, 1H), 8.63 (dd, J = 5.6, 1.5 Hz, 1H), 8.72 (dd, J = 5.6, 1.5 Hz, 1H). IR (KBr), ν: 3480 (w), 3159 (w), 2935 (w), 2884 (w), 2817 (w), 1603 (w), 1475 (w), 1455 (w), 1433 (w), 1254 (m), 1202 (m), 1154 (m), 1031 (s), 810 (w), 762 (w) cm^{-1}. ESI-MS of solution of **6a** in MeOH/H_2O (50:50 v/v): m/z 503.1; calc. $C_{14}H_{18}N_3SO_3{}^{195}Pt$, 503.0.

4.4. Preparation of (dpms)Pt^{II}(C_2H_4NH^{t}Bu-κC,κN), **6b**

A 25 mL Schlenk flask equipped with a magnetic stirring bar was charged with 48.9 mg (84 μmol) of **5b**, and 5 mL of 16.9 mM solution of NaOH in degassed MeOH (84 μmol, 1 equ NaOH) under an argon atmosphere. The Schlenk tube was Teflon-sealed under argon, and the stirred suspension was heated at 50 °C. The starting material dissolved after ~30 min. Heating continued for 12 h to complete the reaction. The product was identified by ESI-MS as azetidine complex **6b**. Two isomers, *cis*- and *trans*-**6b**, were detected in a 6:1 ratio. The crude product contaminated with NaCl was used in oxidation experiments.

^{1}H NMR (CD_3OD, 22 °C, 400 MHz), δ: ***cis*-6b**: 1.00 (vtd, J = 9.2, 2.9 Hz, J_{PtH} = 78 Hz, 1H), 1.15 (s, 9H), 1.25–1.62 (m, 1H; J_{PtH} could not be determined due to overlap with multiplets of the minor isomer), 4.36–4.56 (m, 1H; J_{PtH} could not be determined reliably), 5.09 (ddd, J = 13.0, 9.2, 2.9 Hz, J_{PtH} = 88 Hz, 1H), 5.86 (s, 1H), 7.30 (ddd, J = 7.8, 5.8, 1.6 Hz, 1H), 7.46 (ddd, J = 7.8, 5.8, 1.6 Hz, 1H), 7.81 (vd, J = 7.8 Hz, 1H), 7.84 (vd, J = 7.8 Hz, 1H), 8.04 (td, J = 7.8, 1.6 Hz, 1H), 8.05 (td, J = 7.8, 1.6 Hz, 1H), 8.92 (dd, J = 5.8, 1.6 Hz, 1H), 8.97 (d, J = 5.8 Hz, 1H). ***trans*-6b**: 1.18 (s, 9H), 1.19–1.60 (m, 2H), 4.59–4.75 (m, 1H), 4.94–5.04 (m, 1H), 7.30–7.37 (m, 1H), 7.47–7.52 (m, 1H), 8.49–8.56 (m, 2H), 8.76 (d, J = 6.0 Hz, 1H), 8.86 (d, J = 5.6 Hz, 1H), other peaks of a minor isomer and ^{195}Pt-H coupling constants could not be determined. ESI-MS of solution of **6b** in methanol, m/z 545.1; calc. for M·H$^+$, $C_{17}H_{24}N_3SO_3{}^{195}Pt$ 545.1.

4.5. Oxidation of 6a with H_2O_2 to ***7a*** in methanolic solution

A suspension of **6a** (20.0 mg, 4.0 μmol) in 0.8 mL of CD_3OD was placed into a 10 mL vial equipped with a magnetic stirring bar. A 30% aqueous H_2O_2 solution (4.5 μL, 4.4 μmol, 1.1 equ) was added to the stirred suspension. After a few minutes the starting material completely dissolved and the solution turned yellow. Stirring continued for 1 h at rt. 1,4-dioxane (10 μL) was added as an internal standard. According to ^{1}H NMR spectroscopy, quantitative oxidation occurred. The resulting solution was strongly alkaline. The ratio of two isomers characterized by the signals of the N–Me groups at 2.87 ppm and 2.11 ppm, was 2:5 after 1 h after preparation. The ratio increased slowly to 2:1 after 10 h, which remained unchanged after 1 day.

The NOE experiments exhibited weak positive NOE's between N–Me group and *ortho*-protons of pyridyl of the dpms ligand in both isomers of **7a**.

^{1}H NMR (CD_3OD, 22 °C, 400 MHz), δ: *cis*-**7a**: 2.87 (s, $^3J_{PtH}$ = 27 Hz, 3H), 2.83–2.93 (m, 1H; $^2J_{PtH}$ could not be determined),

3.07–3.27 (m, $^2J_{PtH}$ = 64 Hz, 1H), 4.62–4.73 (m, $^2J_{PtH}$ ~ 64, 1H), 4.86–4.98 (m, 1H), 6.61 (s, 1H), 7.75 (ddd, *J* = 7.7, 5.6, 1.4 Hz, 1H), 7.88 (ddd, *J* = 7.7, 5.4, 1.4 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 8.26–8.32 (m, 2H), 8.76 (dd, *J* = 5.6, 1.4 Hz, $^3J_{PtH}$ = 26 Hz, 1H), 9.02 (d, *J* = 5.4 Hz, $^3J_{PtH}$ = 13 Hz, 1H). *trans*-**7a**: 2.11 (s, $^3J_{PtH}$ = 33 Hz, 3H), 2.64–2.89 (m, 1H; $^2J_{PtH}$ could not be determined), 2.97–3.31 (m, 1H; $^2J_{PtH}$ could not be determined), 4.02–4.28 (br m, 1H), 4.57–4.77 (br m, 1H), 6.70 (s, 1H), 7.79 (ddd, *J* = 7.7, 5.6, 1.5 Hz, 1H), 7.91 (ddd, *J* = 7.7, 5.6, 1.1 Hz, 1H), 8.05–8.11 (m, 2H), 8.25–8.34 (m, 2H), 8.69 (d, *J* = 5.6 Hz, $^3J_{PtH}$ = 27 Hz, 1H), 8.92 (d, *J* = 5.6 Hz, $^3J_{PtH}$ = 14 Hz, 1H). ^{13}C NMR (CD_3OD, 22 °C, 500 MHz), *δ*: *cis*-**7a**: −2.0 ($^1J_{PtC}$ = 414 Hz, Pt–CH_2), 56.0 ($^2J_{PtC}$ = 22 Hz, NMe), 72.3 (m, $CDSO_3$), 80.3 ($^2J_{PtC}$ = 115 Hz, N–CH_2), 128.0, 128.4, 129.2, 130.3, 143.6, 144.4, 149.8, 151.2, 152.6, 152.9 (py). *trans*-**7a**: −5.0 (Pt-CH_2), 39.7 (NMe), 63.8 (N-CH_2), 72.3 (m, $CDSO_3$), 128.6, 128.8, 129.4, 130.1, 144.1, 145.1, 149.7, 151.1, 151.9, 152.5 (py). (J_{PtC} could not be determined). ESI-MS of solution of **7a** in MeOH: *m*/*z* 519.1; calc. M·H$^+$, $C_{14}H_{18}N_3SO_4{}^{195}$Pt 519.1.

4.6. Preparation of (*7a*)$_2$(SO_4)

A sample of **6a** (53.3 mg, 105 μmol), 10 mL of H_2O and 30% H_2O_2 solution (12 μL, 116 μmol) were used as described above. After 1 h the resulting alkaline solution was neutralized with 1 equ of 1.00 N H_2SO_4 (105 μL). The resulting neutral solution of was evaporated under vacuum to produce white crystalline [(dpms)Pt^{IV}(C_2H_4-NMe-*κC*,*κN*)(OH)]$_2$(SO_4). Solid [(dpms)Pt^{IV}(C_2H_4NMe-*κC*,*κN*)-(OH)]$_2$(SO_4) was used for reductive elimination experiments immediately after preparation. According to ^{1}H NMR spectroscopy, two isomers were present in solution in D_2O, presumably *cis*- and *trans*-(**7a**)$_2$(SO_4), in 6:1 ratio. ^{1}H NMR (D_2O, 22 °C, 400 MHz), *δ*: ***cis*-7a**: 2.30 (s, $^3J_{PtH}$ = 33 Hz, 3H), 2.91 (m, $^2J_{PtH}$ = 62 Hz, 1H), 3.27 (m, $^2J_{PtH}$ = 80 Hz, 1H), 4.03 (m, 1H), 5.09 (m, 1H), 6.78 (s, 1H), 7.80 (ddd, *J* = 7.8, 5.7, 1.4 Hz, 1H), 7.92 (ddd, *J* = 7.8, 5.4, 1.1 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.30–8.37 (m, 2H), 8.62 (d, *J* = 5.7 Hz, $^3J_{PtH}$ = 26 Hz, 1H), 8.85 (d, *J* = 5.4 Hz, $^3J_{PtH}$ = 13 Hz, 1H); ***trans*-7a**: 2.46 (s, $^3J_{PtH}$ = 33 Hz, 3H), 2.94–3.44 (m, 2H), 4.42–4.51 (m, 1H), 6.76 (s, 1H), 7.85–7.99 (m, 2H), 8.15–8.24 (m, 2H), 8.28–8.37 (m, 2H), 8.64 (d, *J* = 5.4 Hz, 1H), 8.90 (d, *J* = 5.4 Hz, 1H).

4.7. Preparation of (*7b*)Cl

The solution of crude **6b** containing 1 equ of NaCl in MeOH was prepared by heating **5b** (126 mg, 217 μmol) and 1 equivalent of NaOH in 13 mL of MeOH at 50 °C for 14 h as described above and was used without isolation of **6b**. A 30% aqueous solution of H_2O_2 (282 mg, 2.49 mmol, 11 equ) was added to the stirred solution of **6b.** The reaction mixture turns immediately bright yellow; stirring continued for 30 min. According to ^{1}H NMR spectroscopy, **(7b)**Cl formed quantitatively as the only product. The resulting solution was reduced in volume to 1 mL under vacuum and was left to crystallize at −20 °C overnight. Large colorless crystals were filtered off, washed with cold methanol and dried under vacuum to give 53.3 mg of the product. The filtrate was evaporated to a volume of 0.2–0.3 mL and left at −20 °C for overnight. The crystalline product, (**7b**)Cl·MeOH, was filtered off and washed with small amount of cold methanol to give an additional fraction of white crystals, 34.0 mg. Combined yield 87.3 mg (139 μmol), 64%. Colorless crystalline solid, perfectly soluble in methanol, water and DMSO, slightly soluble in THF.

^{1}H NMR (dmso-d_6, 22 °C, 400 MHz), *δ*: 1.15 (s, 9H), 2.89 (m, $^2J_{PtH}$ = 75 Hz, 1H), 2.94 (m, $^2J_{PtH}$ = 70 Hz, 1H), 3.16 (d, *J* = 5.3 Hz, 3H, MeOH), 4.10 (q, *J* = 5.3 Hz, 1H, MeOH), 4.25 (br s, 1H, OH), 4.41 (m, $^3J_{PtH}$ = 35 Hz, 1H), 4.58 (m, $^3J_{PtH}$ = 40 Hz, 1H), 7.01 (s, 1H), 7.60 (br s, $^2J_{PtH}$ = 58 Hz, 1H, NH), 7.85 (ddd, *J* = 7.9, 5.9, 1.3 Hz, 1H), 7.91 (ddd, *J* = 7.9, 5.5, 1.0 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 8.33 (td, *J* = 7.9, 1.4 Hz, 1H), 8.39 (td, *J* = 7.9, 1.2 Hz, 1H), 8.83 (d, *J* = 5.9 Hz, 1H), 9.48 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (dmso-d_6, 22 °C, 500 MHz), *δ*: −4.1 ($^1J_{PtC}$ = 376 Hz, Pt-CH_2), 25.2 (C–CH_3), 48.5 (CH_3, MeOH), 54.3 ($^2J_{PtC}$ = 114 Hz, N–CH_2), 60.2 (C quat, *t*-Bu), 69.3 ($CHSO_3$), 126.1, 127.3, 127.4, 128.5, 142.6, 143.8 (CH, py), 149.9 (C quat, py), 150.2, 150.3 (CH, py), 150.4 (C quat, py). IR (KBr), *ν*: 3550 (w br), 3267 (w br), 3018 (w), 2971 (w), 2923 (w), 2813 (w), 1607 (w), 1477 (w), 1441 (w), 1308 (m), 1299 (m), 1204 (w), 1144 (s), 1068 (w), 1029 (w), 959 (m), 768 (m), 697 (m) cm^{-1}. ESI-MS of solution of **(7b)**Cl in MeOH: *m*/*z* 561.1; calc. for cationic **7b**, $C_{17}H_{24}N_3SO_4{}^{195}$Pt, 561.1. X-ray quality crystals were obtained by slow crystallization from concentrated methanolic solution at −20 °C.

Anal. Calc. for $C_{18}H_{28}ClN_3O_5PtS$: C, 34.37; H, 4.49; N, 6.68. Found: C, 34.45; H, 4.73; N, 6.36%.

Table 1 lists the key parameters of the single crystal X-ray structure determination for (**7b**)Cl·MeOH.

4.8. Preparation of (*7b*)$BAr^F{}_4$

A 50 mL flask equipped with a magnetic stirring bar was charged with (**7b**)Cl·MeOH (39.0 mg, 62 μmol), $NaBAr^F{}_4$ (54.5 mg, 61 μmol) and 10 mL of CH_2Cl_2. The reaction mixture was stirred under for 1 h at room temperature. Initially insoluble starting material (**7b**)Cl*MeOH dissolved after 1 h and NaCl precipitated from solution. The reaction mixture was filtered from NaCl through Celite, washed with small amount of CH_2Cl_2 and dried under vacuum for 1 day. The product was isolated as white solid, perfectly soluble in CH_2Cl_2 and THF. Yield 63.4 mg (44.5 μmol), 72%.

^{1}H NMR (THF-d_8, 22 °C, 400 MHz), *δ*: 1.26 (s, 9H), 2.87 (m, $^2J_{PtH}$ = 68 Hz, 1H), 3.15 (m, $^2J_{PtH}$ = 81 Hz, 1H), 3.44 (s, $^2J_{PtH}$ = 27 Hz, 1H, OH), 4.56–4.78 (m, 2H), 5.92 (br s, $^2J_{PtH}$ = 74 Hz, 1H, NH), 6.49 (s, 1H), 7.57 (s, 4H), 7.72–7.85 (m, 10H), 7.98–8.06 (m, 2H),

Table 1
Crystal structure data and structure refinement for (**7b**)Cl·MeOH.

Empirical formula	$C_{18}H_{28}ClN_3O_5PtS$
Formula weight	629.03
Crystal size (mm^3)	0.32 × 0.15 × 0.10
Crystal habit	colorless prism
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.5764(6)
b (Å)	10.0716(6)
c (Å)	12.8674(8)
α (°)	92.272(1)
β (°)	102.071(1)
γ (°)	114.844(1)
Volume (Å^3)	1089.87(12)
Z	2
Density (ρ_{calc}) (g/cm^3)	1.917
Absorbtion coefficient (μ) (mm^{-1})	6.690
F(0 0 0) (ē)	616
θ Range for data collection (°)	2.25–27.50
Index ranges	$-12 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 16$
Number of reflections collected	23101
Number of independent reflections	4988
Number of observed reflections [$I > 2\sigma(I)$]	4904
Coverage of independent reflections (%)	99.6
Final *R* indices	R_1, $I > 2\sigma(I)$ 0.0213 wR_2, all data 0.0529 R_{int} 0.0288 R_{sig} 0.0256

8.27 (td, J = 7.8, 1.4 Hz, 1H), 8.31 (td, J = 7.7, 1.4 Hz, 1H), 8.79 (dd, J = 6.0, 1.4 Hz, $^3J_{PtH}$ = 34 Hz, 1H), 9.16 (d, J = 5.4 Hz, 1H).

4.9. Oxidation of **6a** and **6b** with O_2 in neutral, basic, and acidic solutions

Solid samples of crude isolated complexes **6a** or **6b** were dissolved in D_2O or CD_3OD to generate 9–9.4 mM solutions. The resulting solutions were combined with 10 μL 1,4-dioxane used as an internal standard and an additive of an acid (1 M H_2SO_4 or 50 wt.% HBF_4) or a base (as 0.1 M NaOH solution) or were used without additives. The resulting solutions were placed into 10 mL flasks equipped with a magnetic stirring bar. The air was replaced with O_2 and vigorous stirring continued at room temperature. For aerobic oxidation experiments, the reaction mixtures were stirred vigorously under air.

No changes were observed in ^{1}H NMR spectra of the neutral reaction mixtures in D_2O or CD_3OD containing **6a** or **6b** after 2–24 h under O_2 or in the presence of 0.2 equivalents of NaOH after 4 days of stirring under O_2 atmosphere.

Oxidation of **6a** to form **7a** was observed in D_2O solution in the presence of 1 equivalent of HBF_4 or H_2SO_4 as an acid source. The yield of **7a** after 2 h was 93 ± 2%. Slower oxidation was seen under air to give **7a** in 92 ± 2% yield (an average of 2 runs) after 24 h.

Oxidation of **6b** to **7b** was observed in CD_3OD solution with a half-live of ~2 h at 20 °C. After 24 h **7b** formed in 73 ± 2% yield, according to ^{1}H NMR spectroscopy.

Oxidation of **6b** in the presence of 1 equ. HBF_4 in D_2O solution under 1 atm O_2 occurred with a half life of 2.4 h at 20 °C; yield of **7b** after 24 h is 80%.

4.10. Preparation of (dpms)Pt^{IV}(C_2H_4NHt-Bu-κC,κN)(OH), **9b**

A 25 mL round-bottom flask equipped with a magnetic stirring bar was charged with **(7b)**BAr^F_4 (63.4 mg, 44 μmol), 5.2 mg of *t*-BuOK (44 μmol, 1 equ) and 5–6 mL of dry degassed THF. The resulting solution turned yellow immediately after addition of *t*-BuOK; stirring continued for 1 h. After 1 h solvents were removed and the yellow solid was dried under vacuum for 1 day. The product was obtained as yellow crystalline solid, 62.1 mg. The product was used as a mixture with 1 equ of $KBAr^F_4$ without separation. Complex **9b** decomposes slowly in THF-d_8 solution at room temperature with a half-life of ~17 h.

^{1}H NMR (THF-d_8, 22 °C, 400 MHz), δ: 1.12 (s, 9H), 2.54 (m, $^2J_{PtH}$ = 67 Hz, 1H), 2.92 (m, $^2J_{PtH}$ = 84 Hz, 1H), 3.23 (br s, 1H, OH), 4.17 (m, $^3J_{PtH=}$ 43 Hz, 1H), 4.35 (m, $^3J_{PtH}$ = 40 Hz, 1H), 6.32 (s, 1H), 7.62–7.71 (m, 2H), 7.91 (d, J = 7.7 Hz, 1H), 7.93 (d, J = 7.7 Hz, 1H), 8.13 (td, J = 7.7, 1.3 Hz, 1H), 8.15 (vt, J = 7.7 Hz, 1H), 8.78 (d, J = 5.6 Hz, $^3J_{PtH}$ = 23 Hz, 1H), 9.02 (d, J = 4.7 Hz, 1H). $KBAr^F_4$: 7.57 (s, 4H), 7.79 (br s, 8H).

4.11. Attempted reductive elimination from **9b** in aprotic solvents

4.11.1. Reaction in THF-d_8

A sample of **9b** (10 mg, 6.8 μmol, as a mixture with 1 equivalent of $KBAr^F_4$) was dissolved in 0.7 mL of dry degassed THF-d_8, and the resulting yellow solution was placed into an NMR Young tube; [9b] = 9.8 mM. The reaction mixture was heated at 60 °C under an argon atmosphere and periodically analyzed by ^{1}H NMR. The signals of starting material disappear with a half-life of 22 h at 60 °C to produce insoluble products. After 4 days at 60 °C no **9b** remained in solution, and insoluble reaction products were dissolved in MeOH or dmso-d_6.

In dmso-d_6 solution of decomposition products, the complex **6b** was detected by ^{1}H NMR spectroscopy and identified by comparison with ^{1}H NMR spectrum of authentic sample of **6b**. ESI-MS of acidified methanolic solution of the decomposition products revealed the presence of a strong signal, characterized by m/z 545.1, corresponding to **6b**·H^+ (calc. $C_{17}H_{24}N_3SO_3{}^{195}Pt$ 545.1). Low intensity peaks were detected by ESI-MS, characterized by m/z 561.1 and 480.0.

4.11.2. Reaction in CD_2Cl_2 and C_6D_6

A solution of 15 mg of **9b** in 0.7 mL CD_2Cl_2 ([**9b**] = 15 mM) is stable after 3 days of heating at 60 °C in a sealed Young tube.

The suspension of partially soluble **9b** (8 mg, 5 μmol) in C_6D_6 was heated in a sealed Young tube at 60 °C for 25 h. The resulting reaction mixture was evaporated to dryness, re-dissolved in dmso-d_6 and analyzed by ^{1}H NMR. The presence of complex mixture of unidentified products along with **6b** (in 18% yield) and unreacted **9b** (31%) was observed by ^{1}H NMR spectroscopy. The yields of **6b** and **9b** were estimated by integration of $CHSO_3$ singlets at 5.82 ppm and 6.99 ppm, respectively, using BAr^F_4 peaks as an internal standard.

4.12. Reductive elimination from (**7a**)$_2(SO_4)$ in acidic D_2O solutions

A sample of (**7a**)$_2(SO_4)$ (10.8 mg, 17 μmol, *cis*-/*trans*- mixture in 6:1 ratio) was dissolved in 0.8 mL of D_2O and acidified with 1 equivalent of HBF_4 (4 μL of 50% wt. aq. HBF_4, 17 μmol). The resulting solution was placed into an NMR Young tube and ^{1}H NMR spectra of the reaction solution were recorded before reaction and then in regular intervals during heating at 100 °C. Formation of protonated *N*-methyl ethanolamine, $HOC_2H_4NH_2Me^+$ (**8a**), was detected by ^{1}H NMR, identified by comparison of ^{1}H NMR spectrum with an authentic sample. Another product, (dpms)$Pt^{II}(OH_2)_2^+$, described earlier [11], was detected by ^{1}H NMR spectroscopy as the main Pt-containing species after 33 h at 100 °C. Small amounts of solid (dpms)$_2Pt^{II}_2(\mu\text{-}OH)_2$ formed after 33 h. The product dissolves in 0.8 mL of D_2O in the presence of 20 μL of 50 wt.% HBF_4 at 100 °C to give (dpms)$Pt^{II}(OH_2)_2^+$ as the sole product, detected by ^{1}H NMR spectroscopy.

4.12.1. $HOCH_2CH_2NH_2Me^+$·(**8a**)

^{1}H NMR (D_2O/HBF_4, 22 °C, 400 MHz): 2.74 (s, 3H), 3.16 (m, AA′XX′, 2H), 3.83 (m, AA′XX′, 2H).

Intermediate B was characterized by the following set of signals in ^{1}H NMR spectrum in D_2O: 2.48 (s, 3H), 2.55–2.70 (m, 1H), 3.04–3.15 (m, 1H), 3.86–3.94 (m, 1H), 3.96–4.06 (m, 1H), 8.71 (d, J = 6.0 Hz, *ortho*-H of py), 8.94 (d, J = 6.0 Hz, *ortho*-H of py). Other peaks could not be seen due to overlap with resonances of **7a** and other reaction products. ESI-MS analysis of an analogous reaction mixture after heating at 100 °C for 5 h in H_2O/H_2SO_4 solution exhibited new signals at m/z 537.1 that match the calculated pattern expected for [(dpms)Pt^{IV}($CH_2CH_2NH_2Me$)$(OH)_2$]$^+$ (calc. m/z 537.1 for $C_{14}H_{20}N_3O_5S^{195}Pt$).

The graphs of concentration of **7a** (filled circles), **B** (empty rhombs) and **8a** (filled triangles) *vs.* time and the graph in coordinates ln ([**7a**]$_{initial}$/[**7a**]) versus time are given in the Supporting Information, Fig. 11. Concentrations of **7a**, **B**, and **8a** were calculated by integration of N–Me group of isomeric complexes **7a** at 2.46 ppm and 2.30 ppm, CH_2-multiplet of **B** at 3.86–4.06 ppm and a multiplet of **8a** at 3.83 ppm, using residual HDO peak as an internal standard. The estimated 1st order rate constant of disappearance of **7a** at 100 °C is (6.0 ± 0.3) 10^{-5} s^{-1}.

4.12.2. Reductive elimination from (**7b**)Cl in neutral and acidic D_2O solutions

A solution of 3.7 mg of (**7b**)Cl (3.7 mg, 6 mol) in 0.7 mL D_2O was placed into an NMR Young tube and was heated at 100 °C. The reaction was monitored by ^{1}H NMR spectroscopy. The complex (**7b**)Cl disappeared with a half-life 21 h. An intermediate species

appeared in the beginning of reaction and eventually disappeared after prolonged heating, characterized by a multiplet at 3.87–3.97 ppm. After 5 days at 100 °C (**7b**)Cl has completely disappeared. The organic product of the reaction was identified as **8b** by comparison of its ^{1}H NMR spectrum with an authentic sample. The yield of **8b** is 65% based on integration of a multiplet at 3.83 ppm and using residual solvent peak as a standard. Insoluble $(dpms)_2Pt_2(\mu\text{-}OH)_2$ was another reaction product. The solid dissolved upon heating in the presence of a large excess HBF_4 to form $[(dpms)Pt(H_2O)_2]^{2+}$ [11].

*4.12.3. $HOCH_2CH_2NH_2t\text{-}Bu^+$ (**8b**)*

^{1}H NMR (D_2O, 22 °C, 400 MHz): 1.38 (s, 9H), 3.16 (m, AA'XX', 2H), 3.83 (m, AA'XX', 2H).

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Appendix A. Supplementary material

CCDC 797450 contains the supplementary crystallographic data for (**7b**)Cl MeOH. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. ^{1}H and ^{13}C NMR spectra of compounds **6a**, **6b** and **7b** and kinetic characterization for the C–O reductive elimination from **7a** in acidic aqueous solutions can be found, in the online version, at doi:10.1016/j.ica.2010.09.057.

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