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Synthesis, characterization, and acid–base properties of (N–N)Pt^{IV}(CH$_3$)$_2$(OH)$_{2-x}$(OCH$_3$)$_x$ (x = 0, 1) complexes†

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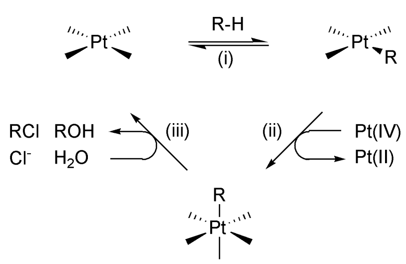
(N–N)Pt^{IV}(CH$_3$)$_2$(OH)$_{2-x}$(OCH$_3$)$_x$ (x = 0, 1; N–N = bipy, 4,4′-(CH$_3$)$_2$bipy, 4,4′-^{t}Bu$_2$bipy, ArN=C(CH$_3$)–C(CH$_3$)=NAr (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$, 3,5-(CH$_3$)$_2$C$_6$H$_3$, 2,6-(CH$_3$)$_2$C$_6$H$_3$) complexes have been prepared by oxidation of the appropriate (N–N)Pt^{II}(CH$_3$)$_2$ complexes using H$_2$O$_2$/H$_2$O. In methanol, the hydroxo–methoxy complexes are formed (x = 1), whereas in acetone, the dihydroxo complexes are formed (x = 0). A single-crystal X-ray structure determination establishes the structure of (4,4′-(CH$_3$)$_2$bipy)Pt^{IV}(CH$_3$)$_2$(OH)$_2$ as a dihydroxo compound with octahedral geometry, with the hydroxo ligands occupying apical coordination sites. The acidities of the protonated bipy hydroxo complexes, (4,4′-R$_2$bipy)Pt^{IV}(CH$_3$)$_2$(OH)(OH$_2$)$^+$ cations, were determined in methanol. The acidities closely matched that of Cl$_2$CHCOOH (pK_a = 6.38 in CH$_3$OH).

Introduction

Selective catalytic functionalization of alkanes is an attractive process that continues to pose major challenges to chemists. Progress in the field has been made during the last decades, but only a few protocols can be employed in order to catalytically oxidize methane to value-added products.[1] One applicable catalyst is the classical Shilov system.[2] It comprises aqueous platinum salts, and can be used to convert various hydrocarbons into their corresponding alcohols or alkyl chlorides, albeit with limited catalytic efficiency. Several studies aimed at a deeper understanding of the underlying principles of the Shilov system have been reported,[1] and the catalytic cycle is generally described by three steps: (*i*) C–H activation, (*ii*) oxidation of Pt(II) to Pt(IV), and (*iii*) reductive elimination of the functionalized hydrocarbon with concomitant regeneration of the active Pt(II) species, as outlined in Scheme 1. In the search for alternative oxidants to the rather impractical Pt(IV) salts used in the original studies,[2] various alternatives have been studied, *e.g.* dioxygen,[3,4] chlorine,[5] and peroxydisulfate.[6] For all of these oxidants, the turnovers are too low for practical applications.



Scheme 1 Schematic presentation of the key steps involved in the catalytic Shilov cycle.

Recently, hydrocarbon C–H activation was found to occur under mild conditions at the cationic species obtained by protonation of (diimine)Pt^{II}(CH$_3$)$_2$ with aqueous HBF$_4$ in trifluoroethanol,[7] and the mechanism of this particular C–H activation process has been studied in detail.[8] In an extension of these studies, and relevant to the oxidation step in the Shilov cycle, *i.e.* step (*ii*) in Scheme 1, we would now like to report on the oxidation of various neutral (N–N)Pt^{II}(CH$_3$)$_2$ complexes. The oxidation products are described as (N–N)Pt^{IV}(CH$_3$)$_2$(OH)$_{2-x}$(OCH$_3$)$_x$, where x = 0, 1 and depends on the chosen solvent. (N–N) symbolizes various diimine and 4,4′-substituted bipyridine ligands (4,4′-R$_2$bipy). The formation of closely related (tmeda)Pt^{IV}(CH$_3$)$_2$(OH)(OCH$_3$) complexes arising from the oxidation of (tmeda)Pt^{II}(CH$_3$)$_2$ with O$_2$ in methanol has been recently described.[4] The oxidation of some (diimine)Pt(CH$_3$)$_2$ complexes with O$_2$ was also discussed but details concerning the products were not given.[4]

† Based on the presentation given at Dalton Discussion No. 6, 9–11th September 2003, University of York, UK.

Results and discussion

The Pt(II) complexes **1**–**6** (Scheme 2) were conveniently prepared from Pt$_2$(CH$_3$)$_4$(μ$_2$-S(CH$_3$)$_2$)$_2$[9] and the appropriate 4,4′-R$_2$bipy or diimine.[7]

Oxidation of (N–N)Pt^{II}(CH$_3$)$_2$ with H$_2$O$_2$/H$_2$O

Oxidation of **1**–**6** can be performed with H$_2$O$_2$/H$_2$O to rapidly and cleanly afford various Pt(IV) complexes as either the dihydroxo complexes **7**–**11** or the hydroxo–methoxy complexes **12**–**17**. The choice of solvent is the key to a controlled product formation, as illustrated in Scheme 2. In acetone, only dihydroxo complexes are formed, whereas in methanol, hydroxo–methoxy complexes are exclusively formed. This important effect of the solvent was independent of the chelating (N–N) ligands employed. All reactions could be successfully performed at room temperature, except the preparation of **10** and **11** which had to be done at lower temperature (−30 °C to −10 °C) due to rapid decomposition of the products under the reaction conditions at ambient temperature. The bipy-supported oxidation products **7**–**9** and **12**–**14** were stable towards air and light, whereas the diimine analogues **10** and **11** and **15**–**17** were air- and light sensitive. A downfield shift of the ^{1}H NMR Pt–CH_3 resonance and a lowering of the ^2J(PtH) coupling constant was observed for the Pt(II) to Pt(IV) oxidation, as expected. Only minor differences in the chemical shifts and coupling constants were observed between the dihydroxo and the hydroxo–methoxy complexes, and they do not appear to reflect any significant differences in the nature of these species.

In the ^{1}H NMR spectra, the C_s symmetry of all the new compounds **7**–**17** is reflected in the single Pt–CH_3 ^{1}H NMR resonance with their characteristic ^2J(^{195}PtH) satellites. The most significant differences between the (4,4′-R$_2$bipy)Pt(IV) and (diimine)Pt(IV) complexes are seen in the Pt–CH_3 ^{1}H NMR shifts. In the (4,4′-R$_2$bipy)Pt(IV) complexes, they are found in the range 1.68–1.74 ppm whereas in the (diimine)Pt(IV) complexes, they are found further upfield in the range 1.07–1.19 ppm. The ^2J(PtH) values are all in the range 69.3–73.5 Hz, with

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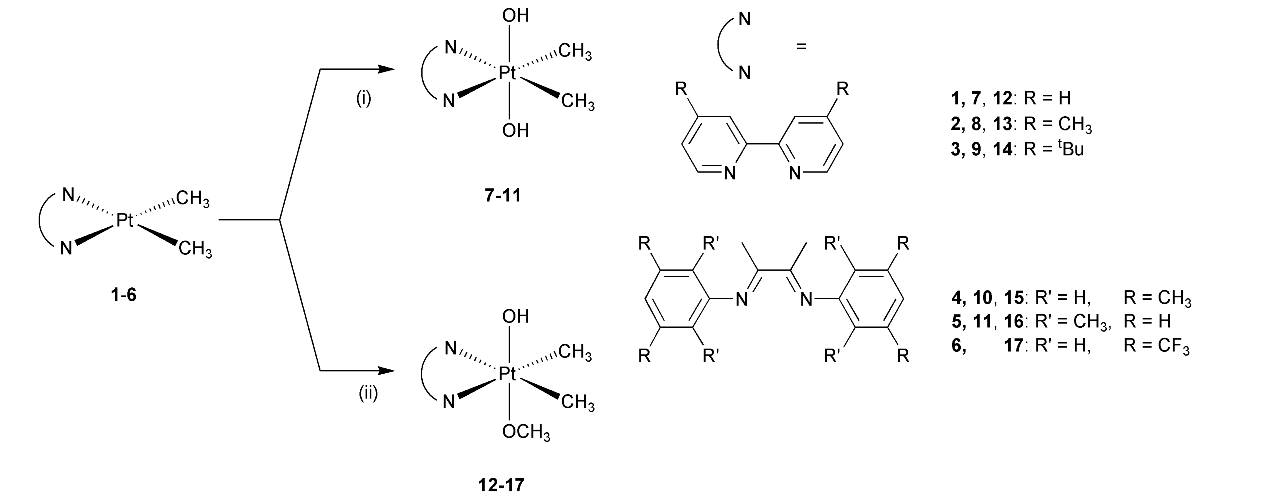


Scheme 2 Preparation of (N–N)Pt^{IV}(CH_3)$_2$(OH)$_{2-x}$(OCH_3)$_x$ (x = 0,1). Reagents and conditions: (*i*) H_2O_2/H_2O, acetone; (*ii*) H_2O_2/H_2O, CH_3OH.

Table 1 Selected geometric parameters (bond lengths in Å, angles in °) in **8**·2CH_3OH

Pt(1)–C(13)	2.040(2)	Pt(1)–N(2)	2.158(2)
Pt(1)–C(14)	2.040(2)	Pt(1)–O(1)	2.018(2)
Pt(1)–N(1)	2.150(2)	Pt(1)–O(2)	2.015(2)
O(1)–Pt(1)–O(2)	177.2(1)	O(1)–Pt(1)–N(2)	91.2(1)
O(1)–Pt(1)–C(13)	91.3(1)	C(13)–Pt(1)–C(14)	86.4(1)
O(1)–Pt(1)–C(14)	90.9(1)	C(13)–Pt(1)–N(1)	97.9(1)
O(1)–Pt(1)–N(1)	89.1(1)	C(13)–Pt(1)–N(2)	173.7(1)

no systematic differences between the complexes. $^{13}C\{^1H\}$ NMR spectra show single Pt–CH_3 signals, together with diagnostic ^1J(PtC) satellites, in agreement with the symmetry of the products. The Pt–CH_3 $^{13}C\{^1H\}$ NMR resonances are found slightly upfield from $SiMe_4$, where typical values are in the range −3.5 to −3.8 ppm (^1J(PtC) = 644–648 Hz) (**7**–**9**), −1.8 to −2.0 ppm (^1J(PtC) = 667–671 Hz) (**12**–**14**), and −1.1 ppm (**15**).

Methanol-d_4 was found to be a well-suited NMR solvent for our studies, and consequently, O*H* resonances in the complexes could not be observed due to rapid H/D exchange with the solvent. On the other hand, in KBr pellets of **7**–**9** and **12**–**14**, IR absorptions assigned to an O–H stretch were detected, providing support for the proposed structures. Furthermore, in **8**, the OH groups were readily located in the X-ray crystal structure (*vide infra*).

The presence of the methoxy group is confirmed by the Pt–OCH_3 ^{1}H NMR resonance at 2.59–2.62 ppm (**12**–**14**) and 2.78–2.87 ppm (**15**–**17**) with characteristic ^{195}Pt satellites with ^3J(PtH) values in the range 39.2–39.6 Hz (**12**–**14**) and 42.0–43.4 Hz (**15**–**17**). Integration of the Pt–CH_3 and Pt–OCH_3 signals show that they are present in a 6 : 3 ratio. This supports the view that there is one methoxy group attached to each platinum centre. In the $^{13}C\{^1H\}$ NMR spectra, the OCH_3 resonances in **12**–**14** appear at 56.8–56.9 ppm, and 56.1 (**15**). Correlated $^1H/^{13}C$ NMR spectra confirm the assignments of the ^{1}H and ^{13}C resonances of the methoxy groups (**12**–**14**).

X-Ray quality crystals were grown for **8**, and the ORTEP[26] view is given in Fig. 1. Selected bond distances and angles are given in Table 1. To the best of our knowledge, the crystal structure presented herein is the first to be reported for any complex generally described as (4,4′-R_2bipy)Pt^{IV}(CH_3)$_2$(OH)$_2$.[10] The X-ray structure confirms the formulation of **8** as a dihydroxo complex with the OH groups occupying the apical positions with respect to the main coordination plane. Complex **8** cocrystallized with methanol as a 1 : 2 adduct. The X-ray crystal structure shows quite clearly that hydrogen bonding exists and is quite strong between Pt–OH and the cocrystallized $HOCH_3$. This is reflected in the O(2)–O(22) distance of only 2.59 Å. Since **7**, **8**, and **9** only differ in the H *vs.* alkyl

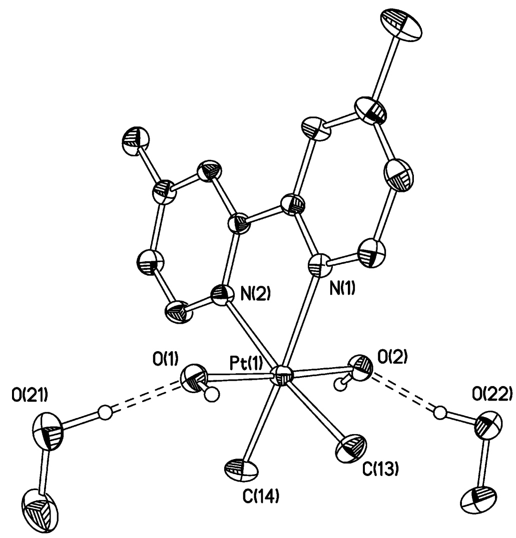


Fig. 1 ORTEP view of **8**·2CH_3OH. Hydrogen atoms, except for OH, have been omitted for clarity. The dotted lines represent hydrogen bonds.

substitution in the 4,4′-position on the bipy ligand and the simple ^{1}H and $^{13}C\{^1H\}$ NMR spectra are similar to those of **8**, it seems reasonable to expect **7** and **9** to be symmetrical dihydroxo compounds with apical hydroxo ligands as well.

Monaghan and Puddephatt have previously reported that the oxidation of **1** can be achieved simply by stirring the compound in either acetone or methanol in the presence of air.[11] Based on conductivity measurements in methanol, the oxidation product in acetone was formulated as a hydroxo–aqua complex, which is in contrast to the solid state structure reported in Fig. 1. It should be noted that the ^{1}H NMR data of **7** differ slightly from those reported for the O_2 oxidation product of **1** in acetone.[11] Particularly noteworthy is the ^{1}H NMR resonance, referenced to residual solvent signals in dichloromethane-d_2, for Pt–CH_3 (^2J(PtH)) observed at 1.59 ppm (72.3 Hz) in **7** *vs.* 1.84 ppm (70 Hz) reported for the hydroxo–aqua complex.[11]

Details concerning the kinetics and mechanisms of the oxidation process outlined in Scheme 2 are beyond the scope of this contribution, so we limit ourselves to mentioning the following. (*i*) When H_2O_2/H_2O was added to the dihydroxo compound **7** in methanol, no reaction was observed. Thus, **7** is not an intermediate in the reaction mechanism in the formation of **12** from **1**. (*ii*) Only a single isomer is formed in either of the two solvents. (*iii*) The hydroxo–methoxy complex is formed in methanol, whereas the dihydroxo species are formed in acetone (containing water). These findings appear to agree with a previously proposed mechanism of these and related oxidations. The mechanism involves axial electrophilic attack by the oxidant at the square planar Pt(II) complex, accompanied by heterolytic cleavage of the oxidant. All of this is possibly assisted by the coordination of a sixth ligand (water or methanol) prior to or in concert with the electrophilic attack, thus completing the octahedral Pt(IV) ML_6 structure.[4,12]

The fact that **7** is not converted to **12** in methanol suggests that dissociation of hydroxide to give pentacoordinate Pt(IV) species does not occur under these conditions. Pentacoordinate Pt(IV) species that are of interest in the context of C–H activation have been recently described.[13] We are currently pursuing the possibility that activation of **7**–**17** with Lewis acids might promote ligand dissociation and formation of related pentacoordinate species.

Oxidation of (4,4′-R$_2$bipy)Pt^{II}(CH$_3$)$_2$ with *meta*-chloroperbenzoic acid (R = H, CH$_3$)

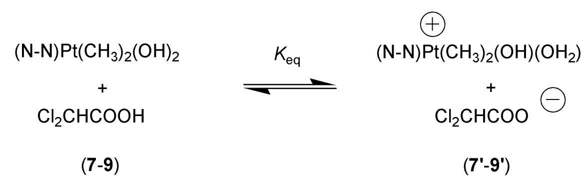
The dimethyl complexes **1** and **2** were oxidized with *meta*-chloroperbenzoic acid (mCPBA) in acetone. The reaction products (**18**, **19**) have the overall composition (4,4′-R$_2$bipy)-Pt(CH$_3$)$_2$(OH)$_2$·(*m*-C$_6$H$_4$Cl(COOH)). These products both showed single Pt–C*H$_3$* ^{1}H NMR resonances in methanol-*d$_4$* at 1.81 ppm (**18**) and 1.77 ppm (**19**), with ^2J(PtH) = 69.6 Hz (**18**) and 69.3 Hz (**19**), respectively. All of these values and the structural implications of the simple ^{1}H NMR spectra compare well to those observed for **7** and **8**. The composition and the expected coordination geometry was unambiguously confirmed by an X-ray diffraction crystal structure investigation for **18**. Unfortunately, the quality of the structure determination was inadequate for an assessment of the finer structural details including bond distances and angles. There were, however, indications of short O ··· O distances that would suggest[14] hydrogen bonding interactions between the carboxylic acid group in *m*-C$_6$H$_4$Cl(COOH) and the Pt–OH groups. The slight upfield shift of the Pt–C*H$_3$* resonances and lowering of ^2J(PtH) in **18** compared to **7**, may also be readily explained by protonation at, or hydrogen bonding interaction with, a Pt–OH group.

It is in line with earlier studies of RO–OR′ oxidative addition to Pt(II) complexes[15] when we find that only the OH groups oxidatively add to the Pt(II) centre, and not the *m*-C$_6$H$_4$Cl-(COOH) fragment. This may be readily understood in terms of the mechanism that has already been outlined for the oxidation reactions, *i.e.* a coordinated solvent molecule (H$_2$O) assists the heterolytic cleavage of the O–O bond in mCPBA. It is the better leaving group, *m*-C$_6$H$_4$Cl(COO$^-$) rather than OH$^-$, that departs during the O–O cleavage.

Brønsted base properties of Pt-bonded hydroxo ligands

The hints at hydrogen bonding interactions may be inferred from the ^{1}H NMR data and in the crystal structure (albeit lacking in quality, as mentioned above) of **18** suggests that the Pt–OH group must have a basicity that is comparable to that of *m*-chlorobenzoate. The pK_a of *m*-chlorobenzoic acid has been determined to be 8.83 in methanol.[16] Prompted by this, we decided to undertake an investigation of the Brønsted base properties of the dihydroxo compounds **7**–**9**. Quantitative studies were performed by ^{1}H NMR in methanol-*d$_4$*.[17] Acidities of Pt(II) diammine and related complexes have been extensively studied by NMR methods,[18,19] but data for Pt(IV) systems are scarce. (We note that a relevant neutral Pt(IV) dimethyl monohydroxy complex was reportedly[14] protonated by dilute HNO$_3$). We found 2,2-dichloroacetic acid (the pK_a of Cl$_2$CHCOOH in methanol is reported to be 6.38[16]) to be well-suited for these studies. A proton-transfer equilibrium was immediately established. The relative acidities allowed for successive additions of controlled amounts of acid with measurable changes in the position of the Pt–C*H$_3$* ^{1}H NMR resonance, observed as a weighted average of the chemical shifts of the protonated and unprotonated Pt species. Details of the experimental procedures and data analysis are given in the Experimental section.

If we assume the equilibrium between the neutral and the protonated complexes to be described by Scheme 3, then an analytical expression for the equilibrium constant K_{eq} may be derived.[17] Fig. 2 illustrates the experimental data and the least-squares-fit of the analytical expression for K_{eq}. We found no significant differences between the pK_a's determined for the three different (4,4′-R$_2$bipy)Pt(IV) species. According to our estimates, the pK_a values of the protonated hydroxo species, **7′**–**9′**, in methanol-*d$_4$* are in the range 6–7, *i.e.* essentially the same as that of the reference acid Cl$_2$CHCOOH. For comparison, the aqueous pK_a for *cis*-Pt(NH$_3$)$_2$(OH)(H$_2$O)$^+$ has been reported to be 7.87.[19] The reason that we provide a rather large uncertainty for the pK_a data is the following. The proton-transfer equilibrium constant with the reference acid was estimated both in the presence and absence of added salts, including PPN$^+$BF$_4^-$ and Cl$_2$CHCOOX/Cl$_2$CHCOOH (X = Na, K) buffers. Without the buffer, K_{eq} was estimated as *ca.* 0.2, independent of whether PPN$^+$BF$_4^-$ was added or not. On the other hand, the presence of the buffer resulted in values of K_{eq} that were up to 10 times greater, depending on the concentration of the buffer, but again independent of whether PPN$^+$BF$_4^-$ was added or not. It appears that the protonated form gains some extra stabilization in the buffered medium, possibly through some specific hydrogen bonding interaction. Alternatively, the differences in the pK_a estimates in the absence and presence of buffer may be caused by the chemical shifts of protonated and/or unprotonated species being slightly dependent on the buffer concentration. Either way, this again may complicate the pK_a determinations. Due to this uncertainty, we choose to report the pK_a values of **7′**–**9′** in methanol to be in the range 6–7.



Scheme 3 Equilibrium between (4,4′-R$_2$bipy)Pt(IV)(CH$_3$)$_2$(OH)$_2$ (**7**–**9**) and their protonated forms (**7′**-**9′**).

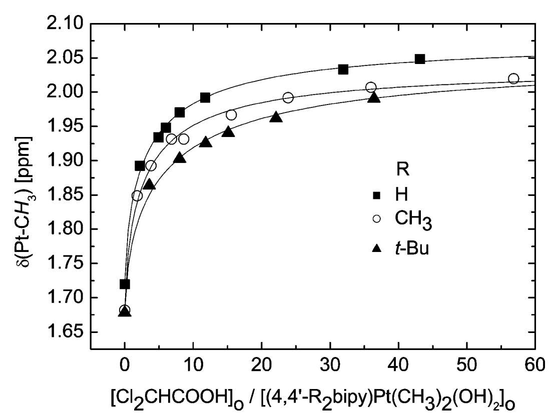


Fig. 2 Pt–C*H$_3$* ^{1}H NMR chemical shifts at various initial ratios between the acid and the (4,4′-R$_2$bipy)Pt^{IV}(CH$_3$)$_2$(OH)$_2$ complex. Fully drawn lines are least-square-fits of the derived analytical expression for K_{eq}.[17]

In the pK_a determination that is based on Scheme 3, we assume that the protonated species and their counter-ions are separate ions pairs. The data in Fig. 2 may in principle be described by an equilibrium between neutral species and associated ion pairs, giving slightly different estimated values for K_{eq} and $\delta_{i'}$ (i′ = **7′**, **8′**, **9′**), but the goodness-of-fits are significantly lower compared to those obtained for the equilibrium given in Scheme 3.[20] In addition, the estimated $\delta_{i'}$ values of 2.02 (**7′**–**9′**) associated ion pairs deviate more from the values obtained by full protonation with HOTf and CF_3COOH than those estimated by treating the right hand side as separate ions (*vide infra*). Thus, if we consider the right hand side of Scheme 3, separate ions are in better agreement with the experimental data than are contact ion pairs.[21]

The protonated species **7′**–**9′** were not isolated, but by extrapolation of the analytical expression for K_{eq}, we were able to extract the Pt–CH_3 ^{1}H NMR chemical shifts of these species in methanol-d_4. The coupling constants ^2J(PtH) in the protonated species were also estimated by extrapolation of a ^2J(PtH) *vs.* initial [acid]/[Pt(IV)] ratio plot similar to Fig. 2. The estimated ^{1}H NMR shift values in methanol-d_4 are: 2.08 ppm (**7′**), 2.04 ppm (**8′**), and 2.05 ppm (**9′**), with ^2J(PtH) approximately equal to 67 Hz. These values are in excellent agreement with the Pt–CH_3 ^{1}H NMR values δ_H 2.09 ppm (^2J(PtH) = 66 Hz) observed by protonation of **7** with 1.6 equivalents of HOTf and δ_H 2.07 ppm (^2J(PtH) = 66 Hz) observed by protonation with 15 equivalents of CF_3COOH. Under these conditions, essentially complete protonation of **7**–**9** was achieved, evidenced by the fact that a further increase of the acid concentrations to 8 equivalents for HOTf or 25 equivalents for CF_3COOH did not change the position of the observed Pt–CH_3 resonances. (A much larger excess of HOTf eventually resulted in decomposition of the complex, possibly by intermediacy of the unobserved diprotonated species, *i.e.* the dicationic Pt(IV) bis(aqua) complexes).

Conclusions

We have demonstrated that several bipy and diimine-based (N–N)Pt(CH_3)$_2$ complexes undergo smooth oxidation with H_2O_2/H_2O and mCPBA to give interesting Pt(IV) hydroxo complexes. The identity of the oxidation product depends on the choice of solvent, where (N–N)Pt(CH_3)$_2$(OH)$_2$ and (N–N)–Pt(CH_3)$_2$(OH)(OCH_3) are obtained in acetone and methanol, respectively. The formation of these products may be rationalized in terms of previously proposed mechanisms. The mechanistic insight will allow for designed syntheses of novel complexes by variation of the two axial ligands. The chemistry of the Pt(IV) complexes is currently being further investigated, and the results will be reported in due time.

Experimental

General considerations

(4,4′-R$_2$bipy)Pt^{II}(CH_3)$_2$ (**1**–**3**) and (diimine)Pt^{II}(CH_3)$_2$ (**4**–**6**) were synthesized in toluene from Pt$_2$(CH_3)$_4$(μ_2-S(CH_3)$_2$)$_2$[9] and the appropriate 4,4′-substituted bipyridine or diimine.[7] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance DXP 300 instrument. The ^{1}H NMR spectra were obtained in CD_3OD, DMSO, or CD_2Cl_2, and the chemical shifts reported are relative to SiMe$_4$, using the residual solvent resonances at δ_H 3.30 ppm, 2.49 ppm, 5.32 ppm as internal references. The ^{13}C NMR spectra were obtained in CD_3OD or $CDCl_3$, the chemical shifts are given relative to SiMe$_4$ and the solvent resonances at δ_C 49.0 ppm and 77.2 ppm were used as internal references. IR spectroscopy was performed on KBr tablets using a Perkin Elmer One Spectrometer. Elemental analyses were performed by Ilse Beetz Microanalytisches Laboratorium, Kronach, Germany. 4,4′-R$_2$bipy (R = H, CH_3, *t*-Bu) was used as received from Sigma-Aldrich, H_2O_2/H_2O (30%), acetone, and methanol were all used as received from Kebo Lab, and mCPBA was used as received from Fluka. 2,2-Dichloroacetic acid was degassed and $Cl_2CHCOOX$ (X = K, Na) were dried under vacuum before use, all were purchased from Sigma-Aldrich.

Synthesis

(bipy)Pt^{IV}(CH_3)$_2$(OH)$_2$ (7). To a yellow suspension of **1** (0.336 g, 0.881 mmol) in acetone was added H_2O_2/H_2O (0.180 ml) while stirring. The solids quickly dissolved and the solution changed colour to light yellow. After 10 minutes, most of the volatiles were removed by evaporation (*attention: peroxides*). The product was precipitated and washed with pentane before drying under vacuum to give the product as a light-yellow powder in 98% yield. Anal. calc. for $C_{12}H_{16}N_2O_2Pt$: C, 34.70; H, 3.88; N, 6.74. Found: C, 32.60; H, 3.99; N, 6.80%. ^{1}H NMR δ_H(CD_3OD) 1.73 (6H, s, *J*(PtH) 70.7 Hz, Pt–CH_3)), 7.83 (2H, ddd, *J* = 7.9, 5.4, 1.1 Hz, Ar–*H*), 8.26 (2H, ddd, *J* = 8.2, 7.9, 1.6 Hz, Ar–*H*), 8.64 (2H, ddd, *J* = 8.2, 1.1, 0.6 Hz (poorly resolved), Ar–*H*), 9.02 ppm (2H, ddd, *J* = 5.4, 1.6, 0.6 Hz, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −3.5 (*J*(PtC) = 648 Hz), 125.2, 128.2, 141.3, 148.6, 156.8. ν(OH) = 3392 cm^{-1} (very broad).

(4,4′-(CH_3)$_2$bipy)Pt^{IV}(CH_3)$_2$(OH)$_2$ (8). Prepared analogous to **7** as a light-yellow product in 82% yield. Anal. calc. for $C_{14}H_{20}N_2O_2Pt$: C, 37.72; H, 4.55; N, 6.32. Found: C, 37.65; H, 4.96; N, 6.38%. ^{1}H NMR δ_H(CD_3OD) 1.68 (6H, s, *J*(PtH) = 70.8 Hz, Pt–CH_3), 2.62 (6H, s, Ar–CH_3), 7.62 (d, 2H, *J* = 5.7 Hz, Ar–*H*), 8.48 (2H, s, Ar–*H*), 8.81 (d, 2H, *J* = 5.7 Hz, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −3.8 (*J*(PtC) = 646), 125.8, 128.7, 147.8, 153.8, 156.7. ν(OH) = 3370 cm^{-1} (very broad).

(4,4′-*t*-Bu$_2$bipy)Pt^{IV}(CH_3)$_2$(OH)$_2$ (9). Prepared analogous to **7** as a light-yellow product in 86% yield. Anal. calc. for $C_{20}H_{32}N_2O_2Pt$: C, 45.53; H, 6.11; N, 5.31. Found: C, 43.21; H, 5.85; N, 6.26%. ^{1}H NMR δ_H(CD_3OD) 1.49 (s, 18H, Ar–^{t}*Bu*), 1.68 (s, 6H, *J*(PtH) = 70.5 Hz, Pt–CH_3), 7.84 (dd, 2H, *J* = 5.7, 1.9 Hz, Ar–*H*), 8.59 (d, 2H, *J* = 1.9 Hz, Ar–*H*), 8.89 (d, 2H, 5.7 Hz, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −3.7 (*J*(PtC) = 644 Hz), 30.7, 36.7, 122.1, 125.2, 148.1, 156.8, 166.2). ν(OH) = 3060 cm^{-1} (very broad).

(N–N)Pt^{IV}(CH_3)$_2$(OH)$_2$ (10) [N–N = Ar–N=C(CH_3)–C(CH_3)=N–Ar; Ar = 3,5-(CH_3)$_2C_6H_3$]. To a deeply red solution of **4** (36.9 mg, 71.3 µmol) in acetone (5 ml) at −30 °C was added H_2O_2/H_2O (42.6 µl) in portions over several hours while raising the temperature slowly to −10 °C. Excess H_2O_2 was quenched with $Na_2S_2O_3$ in H_2O, the volatiles were evaporated, and the residue was washed with pentane before drying under vacuum. The product was isolated as a light brown solid in 54% yield. ^{1}H NMR δ_H(CD_3OD) 1.19 (s, 6H, *J*(PtH) = 69.3 Hz, Pt–CH_3), 2.38 (s, 12H, Ar–CH_3), 2.47 (s, 6H, N–C(CH_3)), 6.73 (s, 4H, Ar–*H*), 7.05 (s, 2H, Ar–*H*). The compound, pure by NMR, failed to give satisfactory elemental analysis data.

(N–N)Pt^{IV}(CH_3)$_2$(OH)$_2$ (11) [N–N = Ar–N=C(CH_3)–C(CH_3)=N–Ar; Ar = 2,6-(CH_3)$_2C_6H_3$]. To a red solution of **5** (0.1088 g, 0.210 mmol) in acetone at −10 °C was added H_2O_2/H_2O (30%, 64 µl). After two hours, the solvent was evaporated while keeping the reaction mixture ice-cold. The residue was washed with pentane before drying under vacuum. The product was isolated as a brown-yellow solid in 61% yield. Anal. calc. for $C_{22}H_{32}N_2O_2Pt$: C, 47.91; H, 5.85; N, 5.08. Found: C, 47.34; H, 6.05; N, 5.15%. ^{1}H NMR δ_H(CD_3OD) 1.10 (s, 6H, *J*(PtH) = 72.2 Hz, Pt–CH_3), 2.29 (s, 12H, Ar–CH_3), 2.37 (s, 6H, N=CCH_3), 6.95–7,20 (m, 6H, Ar–*H*).

(bipy)Pt^{IV}(CH_3)$_2$(OH)(OCH_3) (12). To a yellow suspension of **1** (65.0 mg, 0.17 mmol) in methanol (5 ml) was added H_2O_2/H_2O (16 µl) while stirring. The solution slowly changed colour to light yellow and after 1 h, the volatiles were removed by evaporation. The product was washed with pentane and dried under vacuum to give the product as a light-yellow powder in 85% yield. Anal. calc. for $C_{13}H_{18}N_2O_2Pt$: C, 36.36; H, 4.23; N, 6.52. Found: C, 35.50; H, 4.25; N, 10.27%. ^{1}H NMR δ_H(CD_3-OD) 1.74 (s, 6H, *J*(PtH) = 71.2 Hz, Pt–C*H*$_3$), 2.62 (s, 3H, *J*(PtH) = 39.6 Hz, Pt–OC*H*$_3$), 7.85 (dd, 2H, *J* = 7.5, 4.9 Hz, Ar–*H*), 8.29 (ddd, 2H, *J* = 8.3, 7.5, 1.1 Hz, Ar–*H*), 8.66 (d, 2H, *J* = 8.3 Hz, Ar–*H*), 9.04 (d, 2H, *J* = 4.9 Hz, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −1.8 (*J*(PtC) = 671 Hz), 56.8, 125.3, 128.3, 141.5, 148.5, 156.8. *ν*(OH) = 3350 cm^{-1} (very broad).

(4,4′-(CH$_3$)$_2$bipy)Pt^{IV}(CH$_3$)$_2$(OH)(OCH$_3$) (13). Prepared analogous to **12** as a light-yellow product in 97% yield. Anal. calc. for $C_{15}H_{22}N_2O_2Pt$: C, 39.39; H, 4.85; N, 6.12. Found: C, 38.29; H, 4.56; N, 5.64%. ^{1}H NMR δ_H(CD_3OD) 1.69 (s, 6H, *J*(PtH) = 70.8 Hz, Pt–C*H*$_3$), 2.59 (s, 3H, *J*(PtH) = 39.2 Hz, Pt–OC*H*$_3$), 2.63 (s, 6H, Ar–C*H*$_3$), 7.66 (d, 2H, *J* = 5.7 Hz, Ar–*H*), 8.52 (s, 2H, Ar–*H*), 8.84 (d, 2H, *J* = 5.7 Hz, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −2.0 (*J*(PtC) = 668 Hz), 21.4, 56.8, 125.9, 128.8, 147.8, 154.0, 156.6. *ν*(OH) = 3372 cm^{-1} (very broad).

(4,4′-*t*-Bu$_2$bipy)Pt^{IV}(CH$_3$)$_2$(OH)(OCH$_3$) (14). Prepared analogous to compound **12** as a light yellow powder in 97% yield. Anal. calc. for $C_{21}H_{34}N_2O_2Pt$: C, 46.57; H, 6.33; N, 5.17. Found: C, 44.38; H, 5.85; N, 5.06%. ^{1}H NMR δ_H(CD_3OD) 1.52 (s, 18H, Ar–^{t}*Bu*), 1.70 (s, 6H, *J*(PtH) = 70.0 Hz, Pt–C*H*$_3$), 2.61 (s, 3H, *J*(PtH) = 39.2 Hz, Pt–OC*H*$_3$), 7.88 (dd, 2H, *J* = 5.7 Hz, 1.9 Hz, Ar–*H*), 8.64 (d, 2H, *J* = 1.9 Hz, Ar–*H*), 8.93 (d, 2H, *J* = 5.7 Hz, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −2.0 (*J*(PtC) = 667 Hz), 30.6, 36.7, 56.9, 122.3, 125.4 148.1, 156.8 166.4. *ν*(OH) = 3400 cm^{-1} (very broad).

(N–N)Pt^{IV}(CH$_3$)$_2$(OH)(OCH$_3$) (15) [N–N = Ar–N=C(CH$_3$)–C(CH$_3$)=N–Ar; Ar = 3,5-(CH$_3$)$_2$C$_6$H$_3$]. To a solution of **4** in methanol (5 ml) was added H_2O_2/H_2O (62.5 µl). The volatiles were removed by evaporation, before the product was washed with pentane and isolated as a yellow solid in 30% unoptimized yield. Anal. calc. for $C_{23}H_{34}N_2O_2Pt$: C, 48.84; H, 6.06; N, 4.95. Found: C, 47.07; H, 6.05; N, 5.15%. ^{1}H NMR δ_H(CD_3OD) 1.08 (s, 6H, *J*(PtH) = 72.1 Hz, Pt–C*H*$_3$), 2.37 (s, 18H, Ar–C*H*$_3$, N=CC*H*$_3$), 2.85 (s, 3H, *J*(PtH) = 42.0 Hz, Pt–OC*H*$_3$), 6.38 (s, 4H, Ar–*H*), 7.00 (s, 2H, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −1.1, 21.4, 56.1, 120.0, 129,5, 140.4, 146.4, 177.6.

(N–N)Pt^{IV}(CH$_3$)$_2$(OH)(OCH$_3$) (16) [N–N = Ar–N=C(CH$_3$)–C(CH$_3$)=N–Ar; Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$]. Prepared analogous to **15** as a yellow solid in 36% yield. Anal. calc. for $C_{23}H_{34}N_2O_2Pt$: C, 48.84; H, 6.06; N, 4.95. Found: C, 36.15/36.19; H, 5.16/4.76; N, 4.45/3.10%. The reasons for this poor elemental analysis are unclear. ^{1}H NMR δ_H(CD_3OD) 1.12 (s, 6H, *J*(PtH) = 73.0 Hz, Pt–C*H*$_3$), 2.26 (s, 6H, N=CC*H*$_3$, 2.33 (s, 12H, Ar–C*H*$_3$), 2.78 (s, 3H, *J*(PtH) = 43.4 Hz, Pt–OC*H*$_3$), 7.05–7.21 (m, 6H, Ar–*H*).

(N–N)Pt^{IV}(CH$_3$)$_2$(OH)(OCH$_3$) (17) {N–N = Ar–N=C(CH$_3$)–C(CH$_3$)=N–Ar; Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$]. Prepared analogous to **15** as a yellow solid in 67% yield. Anal. calc. for $C_{23}H_{22}F_{12}N_2O_2Pt$: C, 35.35; H, 2.84; N, 3.58. Found: C, 34.29; H, 2.77; N, 3.63%. ^{1}H NMR δ_H(CD_3OD) 1.07 (s, 6H, *J*(PtH) = 73.5 Hz, Pt–C*H*$_3$), 2.47 (s, 3H, N=CC*H*$_3$), 2.87 (s, 3H, *J*(PtH) = 43.4 Hz, Pt–OC*H*$_3$), 7.83 (s, 4H, Ar–*H*), 8.05 (s, 2 H, Ar–*H*).

Reaction between 1 and mCPBA to give 18. To a solution of **1** (9.5 mg, 24.9 mmol) in acetone was added mCPBA (5.6 mg, 24.4 mmol). After solvent evaporation and washing with diethyl ether, the product was isolated as a white powder in 48% yield. ^{1}H NMR δ_H(DMSO) 1.62 (s, 6H, *J*(PtH = 71.9 Hz), 7.84 (dd, 2H, *J* = 7.8, 5.4 Hz, Ar–*H*), 8.29 (dd, 2H, *J* = 8.3, 7.8 Hz, Ar–*H*), 8.74 (d, 2H, *J* = 8.3 Hz), 8.91 (d, 2H, *J* = 5.4 Hz, Ar–*H*), 7.20–7.40 (m, 2H, Ar–*H* (mCPBA). The compound, pure by NMR, failed to give satisfactory elemental analysis data.

Reaction between 2 and mCPBA to give 19. To an orange solution of **2** (23.0 mg, 56.2 mmol) in acetone (5 ml) was added mCPBA (12.9 mg, 56.2 mmol). After solvent evaporation and washing with diethyl ether, the product was isolated as a white solid in 35% unoptimized yield. ^{1}H NMR δ_H(CD_3OD) 1.77 (s, 6H, *J*(PtH) = 69.3 Hz, Pt–C*H*$_3$), 6.38 (s, 4H, Ar–*H*), 7.00 (s, 2H, Ar–*H*). ^{13}C{^{1}H} NMR $\delta_{C\{H\}}$(CD_3OD) −1.1, 21.4, 56.1, 120.0, 129,5, 140.4, 146.4, 177.6.

Acid–base equilibrium studies

Experimental considerations. All experiments were performed in CD_3OD, which was dried and distilled under N_2 atmosphere and stored over 3Å molecular sieves.[22] A controlled amount of selected complex **7**–**9** was added to a J. Young NMR tube, and CD_3OD was vacuum transferred into the NMR tube. Inside the glovebox, controlled amounts of $Cl_2CHCOOH$ were added using a syringe and the ^{1}H NMR spectra were measured after each addition. The $[Cl_2CHCOOH]_o/[(4,4'\text{-}R_2bipy)Pt^{IV}(CH_3)_2(OH)_2]_o$ ratio was found from the $Cl_2CHCOOH$ and Pt–C*H*$_3$ ^{1}H NMR integrals.

Low-temperature ^{1}H NMR were conducted down to −80 °C in an attempt to observe separate Pt–C*H*$_3$ signals for the two species in equilibrium, but to no avail. Due to the still rapid exchange processes, only one averaged set of signals could be observed.

Mathematical considerations. Assume the observed Pt–C*H*$_3$ ^{1}H NMR chemical shift to be the weighted average between the neutral and the protonated species, *i.e.* $\delta_{obs} = \delta_i + (\delta_{i'} - \delta_i)x_{i'}$, where δ_{obs} is the observed Pt–C*H*$_3$ ^{1}H NMR resonance, $x_{i'}$ is the molar fraction of the protonated species in the equilibrium mixture (i′ = **7′**–**9′**), and δ_i and $\delta_{i'}$ are the ^{1}H NMR resonances of the neutral (**7**–**9**) and the protonated (**7′**–**9′**) species respectively. δ_i is directly observable whereas $\delta_{i'}$ is estimated by the curve fitting. We further consider the equilibrium equation together with the required mass- and charge-balances. The molar fraction $x_{i'}$ can then be expressed as:

$$x_{i'} = \frac{\left[K_{eq}(\alpha+1)\right] - \sqrt{\left[K_{eq}(\alpha+1)\right]^2 - 4\alpha K_{eq}\left(K_{eq}-1\right)}}{2\left(K_{eq}-1\right)}$$

where $\alpha = [Cl_2CHCOOH]_o/[(4,4'\text{-}R_2bipy)Pt(IV)(CH_3)_2(OH)_2]_o$. Thus, by plotting the observed Pt–C*H*$_3$ ^{1}H NMR resonance as a function of the experimental variable *α*, we can estimate K_{eq} and the ^{1}H NMR resonances of the protonated species **7′**–**9′**. *α* was found from the $Cl_2CHCOOH$ and Pt–C*H*$_3$ integrals.

X-Ray crystallographic analysis of compound 8

X-Ray data were collected on a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation (*λ* = 0.710 73 Å). Data-collection method: *ω*-scan, range 0.3°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[23] Absorption corrections were applied by the use of the SADABS program.[24] The structure was determined and refined using the SHELXTL program package.[25] The non-hydrogen atoms were refined with anisotropic thermal parameters; all hydrogen atoms were allowed for as riding atoms.

Crystal data for $C_{14}H_{20}N_2O_2Pt\cdot 2CH_3OH$ (8·2CH$_3$OH). *M* = 507.49, *T* = 105(2) K, triclinic, space group $P\bar{1}$, *a* = 7.2537(5) Å, *b* = 10.9870(9) Å *c* = 12.0195(9) Å, *α* = 81.881(3)°, *β* = 87.298(3)°, *γ* = 74.897(4)°, *V* = 915.50(12) Å^3, *Z* = 2, D_x = 1.841 Mg m^{-3}, *μ* = 7.683 mm^{-1}, collected 19278 reflections, 10219 unique (R_{int} = 0.0246), final *R* indices ($I > 2\sigma(I)$) *R*1 = 0.0273, *wR*2 = 0.0648, *R* indices (all data) *R*1 = 0.0339, *wR*2 = 0.0669.

CCDC reference number 209032.

See http://www.rsc.org/suppdata/dt/b3/b304475k/ for crystallographic data in CIF or other electronic format.

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