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Kinetics and mechanism of cleavage of the oxygen–oxygen bond in hydrogen peroxide and dibenzoyl peroxide by arylplatinum(II) complexes

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Reaction of $[PtAr_2(NN)]$ (Ar = Ph, *p*-MeC_6H_4, *m*-MeC_6H_4 or *p*-$MeOC_6H_4$; NN = 2,2′-bipyridyl or 1,10-phenanthroline) with R_2O_2, in which R = H or C(=O)Ph, gives the platinum(IV) complexes *cis,trans*-$[PtAr_2(OH)_2(NN)]$ or $[PtAr_2(OCOPh)_2(NN)]$ (as a 5 : 1 mixture of *cis,trans* and *cis,cis* isomers), respectively. The kinetics of these oxidative addition reactions in acetone was followed by visible spectrophotometry between 10 and 40 °C. The reactions followed simple second-order kinetics, rate = $k_2[PtAr_2(NN)][peroxide]$, and the rates were insensitive to change of solvent. Activation parameters have been determined and large negative values for $\Delta S^{\neq}$ were obtained. A mechanism is suggested which involves a concerted three-center transition state, followed by homolytic cleavage of the O–O bond and formation of the final products.

Introduction

There has been a great interest in antitumor activity of platinum(IV) complexes, *e.g.* iproplatin ($[Pt(ipa)(OH)_2Cl_2]$, ipa = isopropylamine).[1–11] In this connection, carboxylation of kinetically inert dihydroxoplatinum(IV) complexes with different reagents such as acid anhydrides and acyl chlorides to form bis(carboxylato)platinum(IV) compounds which have useful antitumor activity has recently been of increasing interest.[8–11] One important route to dihydroxoplatinum(IV) complexes is by the oxidative addition of hydrogen peroxide to platinum(II) complexes. Thus, for example *trans* oxidative addition of an HO–OH bond to $[PtMe_2(phen)]$ or $[Pt(C_6F_5)_2(en)]$ gave $[PtMe_2(OH)_2(phen)]$[12] or $[Pt(C_6F_5)_2(OH)_2(en)]$,[10] respectively.

The oxygen–oxygen bond, along with other Group 16–Group 16 bonds (*e.g.* RSe–SeR), should be considered as class A (non-polar or of low polarity) substrate in the oxidative addition reactions.[13,14] Although there are three distinct mechanisms that are proposed for the activation of class A reagents, a *cis*-concerted mechanism is the dominant one. The mechanistic studies of class A oxidative addition substrates are mostly concerned with H–H, C–H or C–C bond activation. Oxidative addition of some S–S or Te–Te bonds to Vaska's compound, $[IrCl(CO)(PPh_3)_2]$, has been kinetically studied and in each case a mechanism has been suggested.[15,16]

This article describes a kinetic study of the oxidative addition of hydrogen peroxide to platinum(II) complexes $[PtAr_2(NN)]$-(Ar = Ph, *p*-MeC_6H_4, *m*-MeC_6H_4 or *p*-$MeOC_6H_4$; NN = 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen)). A comparative kinetic study is also performed with dibenzoyl peroxide and a mechanism is suggested.

The oxidative addition of the electron-rich complexes $[PtMe_2(NN)]$ with a wide variety of reagents has been studied.[14] Also, the oxidative addition of some alkyl halides to the metallacycle analog $[Pt\{(CH_2)_4\}(NN)]$ has recently been reported.[17,18] Due to the electronic and steric problems, the related study on the aryl analogs $[PtAr_2(NN)]$ has been limited to reaction with MeI[19] for which the reactions are some 50–1000 times slower than the corresponding reactions with dialkylplatinum(II) complexes. However, despite the importance of hydrogen peroxide in chemistry, the literature contains no report of any kinetic and mechanistic study of the oxidative addition of this basic reagent, or any other O–O bond containing reagents, to platinum complexes. We found that H_2O_2 and dibenzoyl peroxide reacted with the arylplatinum(II) complexes with rates that could easily be followed spectrophotometrically.

Results and discussion

Synthesis and characterization of the arylplatinum(IV) complexes

The yellow complexes $[PtAr_2(NN)]$ reacted cleanly with an excess of peroxides R_2O_2 (R = H or C(=O)Ph) in acetone at room temperature to form very pale yellow solutions, from which air-stable solid products having the general formula $[PtAr_2(OR)_2(NN)]$ were obtained. When R = H, the products of each reaction contained almost exclusively the *cis,trans* isomer, and only very small traces of the *cis,cis* isomer were in some cases observed. However, when R = C(=O)Ph, a mixture of both isomers was formed and the ratio of the isomers (*cis,trans* : *cis,cis*), which could not be separated, was approximately 5 : 1.

The complexes were characterized by ^{1}H NMR spectroscopy, microanalysis and IR spectroscopy (see Experimental section for necessary details).

The ^{1}H NMR spectrum of $[Pt(p\text{-}MeC_6H_4)_2(OH)_2(phen)]$ is representative of all the products. The value of $^3J(PtH^2)$ (H^2 is an *ortho* proton of phen) in this platinum(IV) complex is 11.4 Hz, which is considerably lower than the corresponding value of 18.6 Hz for the starting platinum(II) complex $[Pt(p\text{-}MeC_6H_4)_2(phen)]$. The *ortho* protons of the aryl ligands (*i.e.* H^o) appeared as only one doublet (due to coupling to H^m with $^3J(H^oH^m)$ = 7.50 Hz) signal. The presence of only one signal indicates that the complex possesses a plane of symmetry as expected for a product of *trans* addition. Again, the $^3J(PtH^o)$ value of 35.20 Hz in this platinum(IV) complex is much lower than the corresponding value of 68.75 Hz for the starting platinum(II) complex. The H^m protons also appeared as only one doublet (with $^3J(H^oH^m)$ = 7.50 Hz) which further confirms the existence of a plane of symmetry. Also only one singlet was observed at δ 2.39 for the Me substituents on the Ar ligands. A broad resonance at δ 1.23 was assigned to the OH groups, since addition of D_2O led to loss of this peak and appearance of a

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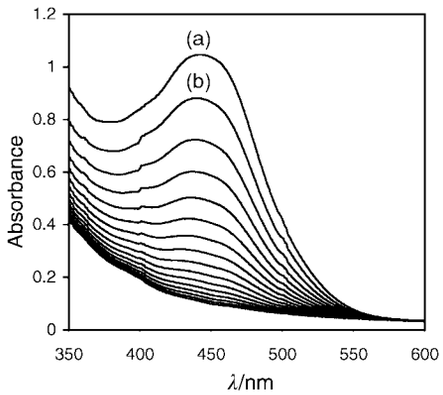


Fig. 1 Changes in the UV–Vis spectrum during the reaction of [Pt(p-$MeOC_6H_4$)$_2$(bpy)] (4.5×10^{-4}M) and H_2O_2 (0.24M) in acetone at T = 20 °C; (a) initial spectrum (before adding H_2O_2) and (b) spectrum at t = 0; successive spectra were recorded at intervals of 30 s.

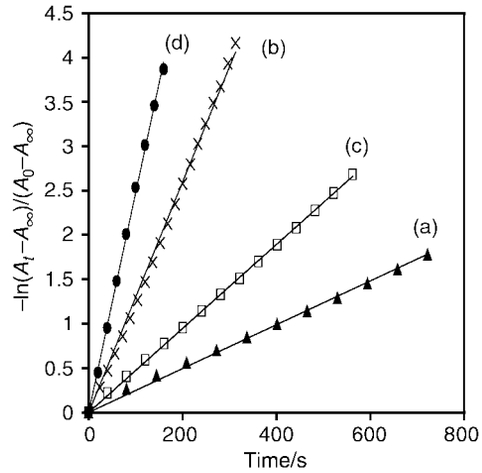


Fig. 2 First-order plots for the reaction of [Pt(p-MeC_6H_4)$_2$(NN)] with peroxides at different temperatures in acetone: (a) H_2O_2 (0.21 M), T = 10 °C, NN = bpy; (b) H_2O_2 (0.21 M), T = 30 °C, NN = phen; (c) dibenzoyl peroxide (0.021 M), T = 20 °C, NN = bpy; (d) dibenzoyl peroxide (0.024 M), T = 40 °C, NN = phen.

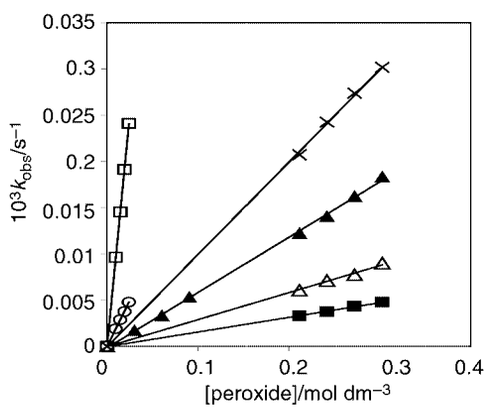


Fig. 3 Plots of first-order rate constants (k_{obs}/s^{-1}) for the reaction of [Pt(p-MeC_6H_4)$_2$(phen)] with H_2O_2 (■, T = 10 °C; △, T = 20 °C; ▲, T = 30 °C; ×, T = 40 °C) and dibenzoyl peroxide (○, T = 10 °C; □, T = 40 °C) in acetone at different temperatures *versus* concentration of peroxide.

peak due to HOD at δ 4.78. Two very small peaks at δ 9.56 and 9.87 were tentatively assigned to the two non-equivalent H^2 protons of the very small trace of the *cis,cis* isomer. The complex also has a strong ν(OH) band in the IR spectrum at 3570 cm^{-1}. In the ^{1}H NMR spectrum of [Pt(p-$MeOC_6H_4$)$_2$(OCOPh)$_2$-(phen)] similar assignments were made to confirm the existence of a plane of symmetry in the *cis,trans* isomer. In addition, three multiplets at δ 8.12 (H^p) and 7.33 and 7.80 (H^m and H^o) were observed for the Ph groups of OC(=O)Ph ligands. Two weaker signals were observed at δ 9.52 and δ 10.20 due to the two non-equivalent H^2 protons of the *cis,cis* minor isomer. For this isomer, two multiplets at δ 7.83 and 7.22 were also clearly observed for non-equivalent *meta* protons of Ar ligands. A singlet at δ 3.85 was assigned to Me substituents of Ar ligands in the *cis,trans* isomer, while for the *cis,cis* isomer the two non-equivalent Me substituents were observed at δ 3.61 and 3.52. Two bands in the IR spectrum of the complex at 1650 cm^{-1} ($\nu_{asym}(CO_2)$) and 1280 cm^{-1} ($\nu_{sym}(CO_2)$) are assigned to the carboxylate coordination (see ref. 10).

The kinetic study

The kinetics of oxidative addition of hydrogen peroxide in acetone (or a 2 : 1 mixture of acetone–benzene) or dibenzoyl peroxide in acetone (or benzene) to [PtAr$_2$(NN)], was studied by using UV–vis spectroscopy. In each case, an excess of peroxide was used and disappearance of the MLCT band at the corresponding λ_{max} (see the Experimental section) was used to monitor the reaction. The change in the spectrum during a typical run is shown in Fig. 1.

The reactions followed good first-order kinetics (Fig. 2). Plots of these first-order rate constants against concentration of the peroxides gave good straight line plots passing through the origin, showing a first-order dependence of the rate on the concentration of peroxides (Fig. 3). The results indicate that the reactions obey a simple second-order rate law [eqn. (1)].

$$-\mathrm{d[PtAr_2(NN)]}/\mathrm{d}t = k_2[\mathrm{PtAr_2(NN)}][\mathrm{peroxide}] \quad (1)$$

The activation parameters were also determined from measurement at different temperatures, and the data are given in Table 1.

The large negative value of $\Delta S^{\neq}$ in each reaction indicates that an association has taken place in the transition state. However, examination of the second-order rate constants upon changing the solvent (from acetone to benzene for the dibenzoyl peroxide reaction and from acetone to a 2 : 1 mixture of acetone–benzene for the hydrogen peroxide reaction) shows that the rate of reactions of Pt(II) complexes with peroxides are not significantly sensitive to a fairly large change in the polarity of the solvent. Thus the possibility of an S_N2-type mechanism in which the transition state involves the formation of a cationic intermediate is not considered. Also, given that these reactions follow good second-order kinetics with remarkable reproducibility and the fact that radical scavengers did not affect the rate would rule out the possibility of any radical mechanism.

We therefore suggest that a concerted three-centered transition state is involved in each of the reactions (Scheme 1). This association is not only consistent with a large negative $\Delta S^{\neq}$ value, but also with the simple second-order rate law given by eqn. (1).

Goddard and Low have presented an elegant *ab initio* model[20–22] for oxidative addition processes in which platinum(II) or platinum(IV) is considered as a neutral atom with a d^{9}s^1 or d^{8}s^2 electronic configuration, respectively. According to this model, the ligands in platinum(II) should significantly distort from square-planar geometry at the transition state to allow the electronic promotion required for the availability of *cis* coordination sites and formation of the six-coordinate transition state (Scheme 1) and eventually the formation of two, new covalent bonds (two Pt–OR) in the six-coordinate platinum(IV) product. Goddard and Low have estimated the Pt(d^{9}s^1 ⟶ d^{8}s^2) transition for the free atom to be endothermic by 17.2 kcal mol^{-1}. If this is taken as an approximate value, then the $\Delta H^{\neq}$ values of approximately 40–50 kJ mol^{-1} (≈10–13 kcal mol^{-1}) for the reactions in Scheme 1 are probably consistent with the

Table 1 Second-order rate constants and activation parameters[a] for reaction of [$PtAr_2(NN)$] with the peroxides (H_2O_2 or $(O_2CPh)_2$) in acetone[b]

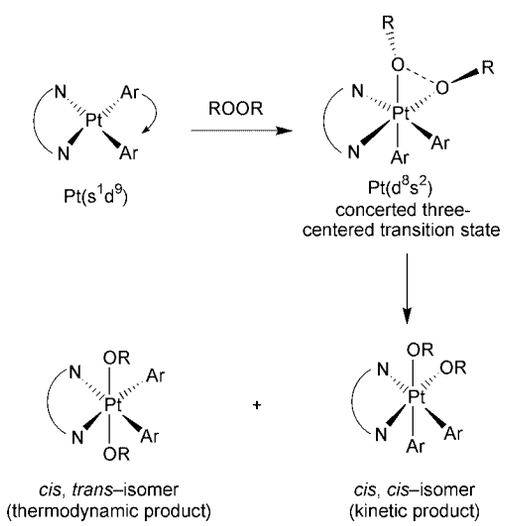
Reaction with H_2O_2

Complex	10^3k_2 (10 °C)/ L mol^{-1} s^{-1}	10^3k_2 (20 °C)/ L mol^{-1} s^{-1}	10^3k_2 (30 °C)/ L mol^{-1} s^{-1}	10^3k_2 (40 °C)/ L mol^{-1} s^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq c}$/J K^{-1} mol^{-1}
[$PtPh_2$(bpy)]	7.8 ± 0.1	19.4 ± 0.1	35.5 ± 0.2	73.7 ± 0.9	51.7 ± 2.4	−102 ± 8
[Pt(*p*-MeC_6H_4)$_2$(bpy)]	12.2 ± 0.1	27.5 ± 0.4	53.5 ± 0.3	90.9 ± 1.1	46.9 ± 2.2	−115 ± 7
[Pt(*p*-MeC_6H_4)$_2$(phen)]	15.7 ± 0.8	34.5 ± 0.3	59.2 ± 0.6	99.8 ± 0.7	42.5 ± 2.5	−128 ± 8
[Pt(*m*-MeC_6H_4)$_2$(bpy)]	11.2 ± 0.1	24.4 ± 0.3	47.2 ± 0.3	89.0 ± 0.6	48.3 ± 7.8	−111 ± 3
[Pt(*p*-$MeOC_6H_4$)$_2$(bpy)]	12.8 ± 0.1	29.1 ± 0.3	55.6 ± 0.4	94.0 ± 0.8	46.5 ± 2.4	−116 ± 8
[Pt(*p*-$MeOC_6H_4$)$_2$(phen)]	17.0 ± 0.1	35.5 ± 0.5	60.6 ± 0.6	102.3 ± 0.9	41.2 ± 1.8	−132 ± 6
	[20.4 ± 0.5]	[40.3 ± 0.3]	[79.9 ± 0.5]	[130.5 ± 0.4]	[43.7 ± 1.6]	[−122 ± 5]

Reaction with $(O_2CPh)_2$

Complex	10^4k_2 (10 °C)/ L mol^{-1} s^{-1}	10^4k_2 (20 °C)/ L mol^{-1} s^{-1}	10^4k_2 (30 °C)/ L mol^{-1} s^{-1}	10^4k_2 (40 °C)/ L mol^{-1} s^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq c}$/J K^{-1} mol^{-1}
[$PtPh_2$(bpy)]	7.5 ± 0.1	14.6 ± 0.1	28.6 ± 0.1	47.5 ± 0.3	43.3 ± 1.3	−113 ± 4
[Pt(*p*-MeC_6H_4)$_2$(bpy)]	11.4 ± 0.1	23.3 ± 0.1	40.5 ± 0.2	64.6 ± 0.5	40.2 ± 2.1	−120 ± 7
	(15.8 ± 0.1)	(28.6 ± 0.1)	(46.2 ± 0.3)	(71.6 ± 0.3)	(34.5 ± 1.1)	(−138 ± 4)
[Pt(*p*-MeC_6H_4)$_2$(phen)]	19.7 ± 0.1	36.3 ± 0.7	59.1 ± 0.8	99.8 ± 0.2	37.0 ± 0.8	−128 ± 3
[Pt(*m*-MeC_6H_4)$_2$(bpy)]	10.8 ± 0.3	21.9 ± 0.6	38.9 ± 0.2	63.7 ± 0.4	41.2 ± 1.6	−117 ± 5
[Pt(*p*-$MeOC_6H_4$)$_2$(bpy)]	13.7 ± 0.1	25.6 ± 0.2	43.2 ± 0.2	69.1 ± 0.6	37.2 ± 1.0	−129 ± 3
	(18.2 ± 0.2)	(32.4 ± 0.2)	(54.6 ± 0.4)	(90.2 ± 0.5)	(36.9 ± 0.2)	(−128 ± 1)
[Pt(*p*-$MeOC_6H_4$)$_2$(phen)]	21.4 ± 0.4	39.5 ± 0.9	61.4 ± 2.9	101.4 ± 3.1	35.2 ± 4.4	−133 ± 8
	(27.3 ± 0.1)	(48.9 ± 0.5)	(79.6 ± 0.5)	(118.9 ± 0.5)	(33.7 ± 1.4)	(−136 ± 5)

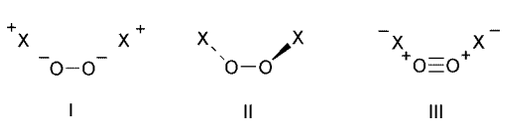
[a] Values given based on 95% confidence limits from least-square regression analysis. [b] Values in square brackets are from a 2 : 1 mixture of acetone–benzene and the values in parentheses are in benzene. [c] Obtained from the Arrhenius equation.



Scheme 1

transition state in each case being "early", *i.e.* the interaction of peroxides with platinum with concomitant weakening of the oxygen–oxygen bond in the transition state is not extensive (considering that the homolytic O–O bond dissociation energy in H_2O_2 is 51.1 kcal mol^{-1}[23]). This "early" transition state may be responsible for the fact that the $\Delta H^{\neq}$ values in the present study are not significantly sensitive to the nature of the incoming peroxide.

Bridgeman and Rothery[24] have presented an *ab initio* model for bonding in halogen and hydrogen peroxides. Thus, for XOOX they have described that when X is H, Br or F, the resonance forms I, II or III (Scheme 2), respectively, are of considerable importance. If this electronegativity effect is extended



Scheme 2

to the ROOR reagents used in the present study, one might predict that the bonding in dibenzoyl peroxide should have a significant contribution from resonance form III, due to the electron withdrawing property of C(=O)Ph groups. It is thus not surprising to observed that dibenzoyl peroxide reacts nearly 10 times faster than hydrogen peroxide with the platinum(II) complexes, if we consider that association of platinum(II) complexes with peroxides to form the three-centered transition state *via* overlapping of the corresponding orbitals proceed by symmetrical platinum attack into the oxygen–oxygen bond. An increase in rate of the reactions of dibenzoyl peroxide on going from acetone solvent to the non-polar solvent benzene, although not great (in fact by a factor of about 1.3), could also be interpreted by this model.

The rates increase slightly with electron-donating substituents on the phenyl ligands (by a factor of about 1.5 from Ph to *p*-$MeOC_6H_4$), probably due to an increased energy of the filled d orbitals which makes the transition Pt($d^9s^1 \longrightarrow d^8s^2$) easier. In the reaction of MeI with [$PtAr_2$(bpy)] complexes[19] which proceeds by an S_N2-type mechanism by a nucleophilic attack of platinum(II) on the carbon atom of the substrate to afford the transient cationic platinum(IV) intermediate, such a rate increase is more pronounced (by a factor of nearly 4 by changing the organic ligand from Ph to *p*-$MeOC_6H_4$). Along the same lines, a slight increase in the rate is observed on going from bpy to phen in the arylplatinum(II) complexes.

One last point remains regarding the stereochemistry of the products. Goddard and Low[22] have pointed out that in Pt(IV) (d^8s^2), electronegative ligands favor bonding to the sp hybride orbital and thus expect that in $Pt(Cl)_2(CH_3)_2(PH_3)_2$ the Pt–Cl bonding favors Pt sp and Pt–CH_3 should favor Pt d, and therefore bonding both Cl to sp orbitals should favor *trans* Cl ligands. Consistent with this, it may not be surprising to observe that the dihydroxy platinum(IV) complexes in the present study have been formed with an almost exclusively *trans* arrangement of the OH groups. (Electronegativities of OH and Cl are close, being 3.16 and 3.42, on the Pauling scale, respectively.[25]) The observation of almost exclusively *trans* oxidative addition is not consistent with the concerted mechanism proposed above (Scheme 1), but it is quite possible that rapid isomerization of

the kinetic *cis* complex to the thermodynamic *trans* complex has occurred.

The related organo-dihydroxoplatinum(IV) complex [PtMe$_2$(OH)$_2$(phen)][12] has also an exclusively *trans* dihydroxy arrangement. The dominant platinum(IV) isomer formed upon oxidative addition of dibenzoyl peroxide to the arylplatinum(II) complexes is also that with *trans* orientation of the OC(=O)Ph ligands (see also ref. 12).

Experimental

The ^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker Avance DPX 250 MHz spectrometer and TMS was used as external reference. All the chemical shift and coupling constants are in ppm and Hz, respectively. UV–vis spectra were recorded using a Philips PU 7850 spectrometer. Kinetic studies were carried out by using a Philips PU 8675 vis spectrometer, fitted with a Pentium (III) computer and with temperature control using a Polyscience 900 constant temperature bath. IR spectra were recorded on a Perkin-Elmer IR 1310 spectrometer as KBr pellets. Melting points were recorded on a Buchi 530 apparatus and are uncorrected. The known complex [PtPh$_2$(bpy)][26] was prepared by a literature method.[27] The following starting materials were prepared similarly with good yields (86–95%) using the corresponding *cis*-[PtAr$_2$(SMe$_2$)$_2$] precurssor[28] and NN. The ^{1}H NMR data are given for two representative complexes and the others gave very similar spectra. The NMR labeling for NN ligands are those that are conventionally used (see for example ref. 17). [Pt(*p*-MeC$_6$H$_4$)$_2$(bpy)]: mp 253 °C (decomp.); λ_{max}/nm: (acetone) 447, (benzene) 484; δ_H 2.25 (6 H, s, ArCH$_3$), 6.85 [4H, d, ^3J(H^{o}H^m) 7.63 Hz, H^m of Ar], 7.40 [4 H, d, ^3J(H^{m}H^o) 7.63 Hz, ^3J(PtH^o) 69.75 Hz, H^o of Ar], 8.70 [1 H, d, ^3J(H^{6}H^5) 5.40 Hz, ^3J(PtH^6) 18.8 Hz, H^6 of bpy], 7.35 [2 H, m, ^3J(H^{5}H^6) 5.40 Hz, H^5 of bpy], 7.99 [2 H, m, ^3J(H^{4}H^3) 8.25 Hz, H^4 of bpy], 8.05 [2 H, d, ^3J(H^{3}H^4) 8.25 Hz, H^3 of bpy]. [Pt(*p*-MeOC$_6$H$_4$)$_2$(phen)]: mp 220 °C (decomp); λ_{max}/nm: (acetone) 438, (2 : 1 mixture of acetone–benzene) 444, (benzene) 484; δ_H 3.80 (6 H, s, ArOCH$_3$), 6.79 [4 H, d, ^3J(H^{o}H^m) 7.65 Hz, H^m of Ar], 7.47 [4 H, d, ^3J(H^{m}H^o) 7.65 Hz, ^3J(PtH^o) 69.26 Hz, H^o of Ar], 9.00 [1 H, d, ^3J(H^{2}H^3) 5.08 Hz, ^3J(PtH^2) 18.6 Hz, H^2 of phen], 8.58 [2 H, d, ^3J(H^{3}H^4) 8.16 Hz, H^4 of phen], 7.98 (2 H, s, H^5 of phen), 7.77 [2 H, dd, ^3J(H^{4}H^3) 8.16 Hz, ^3J(H^{2}H^3) 5.08 Hz, H^3 of phen]. [Pt(*m*-MeC$_6$H$_4$)$_2$(bpy)]: mp 273 °C (decomp.); λ_{max}/nm (acetone): 444. [Pt(*p*-MeOC$_6$H$_4$)$_2$(bpy)] mp 218–222 °C (decomp.); λ_{max}/nm: (acetone) 438, (benzene) 488. The complexes gave satisfactory analytical results.

Syntheses

[Pt(*p*-MeC$_6$H$_4$)$_2$(OH)$_2$(bpy)]. To a solution of [Pt(*p*-MeC$_6$H$_4$)$_2$(bpy)] (50 mg) in acetone (50 ml) was added an excess (1 ml) of 30% w/w hydrogen peroxide in water with stirring. The yellowish solution turned pale yellow. The solvent was removed and the solid residue was recrystallized from acetone–pentane. Yield 80%; mp 220.5 °C (decomp.) (Found: C, 50.3; H, 4.0; N, 5.3. C$_{24}$H$_{24}$N$_2$O$_2$Pt requires C, 50.7; H, 4.2; N, 4.9%); δ_H 1.47 (1 H, br s, OH), 2.36 (6 H, s, ArCH$_3$), 6.97 [4 H, d, ^3J(H^{o}H^m) 7.52 Hz, H^m of Ar], 7.38 [4 H, d, ^3J(H^{m}H^o) 7.52, ^3J(PtH^o) 35.04 Hz, H^o of Ar], 8.82 [2 H, d, ^3J(H^{6}H^5) 5.01 Hz, ^3J(PtH^6) 10.9 Hz, H^6 of bpy], 7.58 [2 H, m, ^3J(H^{5}H^6) 5.01 Hz, H^5 of bpy], 8.07 [2 H, m, ^3J(H^{4}H^3) 8.50 Hz, H^4 of bpy], 8.29 [2 H, d, ^3J(H^{3}H^4) 8.5 Hz, H^3 of bpy]; ν_{max}/cm^{-1}: 3570 (OH).

[Pt(*p*-MeC$_6$H$_4$)$_2$(OH)$_2$(phen)]. This was prepared similarly using [Pt(*p*-MeC$_6$H$_4$)$_2$(phen)]. Yield 80%; mp 261 °C (decomp.) (Found: C, 52.0; H, 4.7, N, 4.0. C$_{26}$H$_{24}$N$_2$O$_2$Pt requires C, 52.8; H, 4.7; N, 4.0%); δ_H 1.23 (1 H, br s, OH), 2.39 (6 H, s, ArCH$_3$), 7.02 [4 H, d, ^3J(H^{o}H^m) 7.50 Hz, H^m of Ar], 7.45 [4 H, d, ^3J(H^{m}H^o) 7.50, ^3J(PtH^o) 35.20 Hz, H^o of Ar], 9.15 [2 H, d, ^3J(H^{2}H^3) 5.06 Hz, ^3J(PtH^2) 11.4 Hz, H^2 of phen], 7.90 [2 H, dd, ^3J(H^{3}H^2) 5.06 Hz, H^3 of phen], 8.57 [2 H, d, ^3J(H^{4}H^3) 8.17 Hz, H^4 of phen], 8.07 (2 H, s, H^5 of phen); ν_{max}/cm^{-1}: 3570 (OH).

The following complexes were made similarly by using the appropriate [PtAr$_2$(NN)] complex. The NN data in the ^{1}H NMR are very similar to those obtained for the above representative complexes and thus are not quoted. [Pt(Ph)$_2$(OH)$_2$(bpy)]. Yield 70%; mp 195 °C (decomp.) (Found: C, 48.7; H, 3.4; N, 4.9. C$_{22}$H$_{20}$N$_2$O$_2$Pt requires C, 48.9; H, 3.7; N, 5.1%); δ_H 1.06 (1 H, br s, OH), 7.50 [4 H, d, ^3J(H^{o}H^m) 7.84 Hz, ^3J(PtH^o) 35.00 Hz, H^o of Ph], 7.15 [4 H, m, ^3J(H^{m}H^o) 7.84, H^m of Ph], 7.20 (2H, H^p of Ph); ν_{max}/cm^{-1}: 3612 (OH). [Pt(*m*-MeC$_6$H$_4$)$_2$(OH)$_2$(bpy)]. Yield 84%; mp 210 °C (decomp.) (Found: C, 49.7; H, 4.1; N, 4.9. C$_{24}$H$_{24}$N$_2$O$_2$Pt requires C, 50.7; H, 4.2; N, 4.9%); δ_H 1.04 (1 H, br s, OH), 2.19 (6 H, s, ArCH$_3$), 7.36 [4 H, ^3J(PtH^o) 35.02 Hz, H^o of Ar], 7.02 (4 H, other H of Ar); ν_{max}/cm^{-1}: 3580 (OH). [Pt(*p*-MeOC$_6$H$_4$)$_2$(OH)$_2$(bpy)]. Yield 94%; mp 173 °C (decomp.) (Found: C, 47.7; H, 4.0; N, 4.4. C$_{24}$H$_{24}$N$_2$O$_4$Pt requires C, 48.0; H, 4.0; N, 4.6%); δ_H 1.90 (1 H, br s, OH), 3.82 (6 H, s, ArOCH$_3$), 6.78 [4 H, d, ^3J(H^{o}H^m) 8.04 Hz, H^m of Ar], 7.42 [4 H, d, ^3J(H^{m}H^o) 8.04, ^3J(PtH^o) 39.23 Hz, H^o of Ar]; ν_{max}/cm^{-1}: 3612 (OH). [Pt(*p*-MeOC$_6$H$_4$)$_2$(OH)$_2$(phen)]. Yield 85%; mp 243 °C (decomp.) (Found: C, 49.7; H, 4.1; N, 4.2. C$_{26}$H$_{24}$N$_2$O$_4$Pt requires C, 50.0; H, 3.9; N, 4.5%); δ_H 1.23 (1 H, br s, OH), 3.85 (6 H, s, Ar-OCH$_3$), 6.83 [4 H, d, ^3J(H^{o}H^m) 8.67 Hz, H^m of Ar], 7.53 [4 H, d, ^3J(H^{m}H^o) 8.67, ^3J(PtH^o) 34.00 Hz, H^o of Ar]. ν_{max}/cm^{-1}: 3612 (OH).

[Pt(Ph)$_2$(OCOPh)$_2$(bpy)]. To a solution of [Pt(Ph)$_2$(bpy)] (40 mg) in acetone (25 ml) was added dibenzoyl peroxide (20 mg) with stirring for 1 h. The yellow solution was decolorized. The solvent was removed and the white solid residue was recrystallized from acetone–pentane. Yield 88%; mp 132 °C (decomp.) (Found: C, 57.4; H, 3.7; N, 3.0. C$_{36}$H$_{28}$N$_2$O$_4$Pt requires C, 57.8; H, 3.7; N, 3.7%); ν_{max}/cm^{-1}: 1760 (asym, CO$_2$) and 1453 (sym, CO$_2$). The ^{1}H NMR data for this and following complexes are not quoted; the data are very similar to the corresponding dihydroxoplatinum(IV) complexes mentioned above expect that in this case three signals close to δ 8.1 (2H), 7.7 (4H) and 7.1 (4H) were in addition observed for Ph groups on C(=O)Ph ligands. Also for the minor product, typical data are given in the main text.

The following complexes were made similarly by using the appropriate [PtAr$_2$(NN)] complex. [Pt(*p*-MeC$_6$H$_4$)$_2$(OCOPh)$_2$(bpy)]. Yield 85%; mp 166 °C (decomp.) (Found: C, 58.1; H, 4.2; N, 3.5. C$_{38}$H$_{32}$N$_2$O$_4$Pt requires C, 58.8; H, 4.2; N, 3.6%); ν_{max}/cm^{-1}: 1660 (asym, CO$_2$) and 1295 (sym, CO$_2$). [Pt(*m*-MeC$_6$H$_4$)$_2$(OCOPh)$_2$(bpy)]. Yield 84%; mp 115 °C (decomp.) (Found: C, 58.1; H, 4.3; N, 3.5. C$_{38}$H$_{32}$N$_2$O$_4$Pt requires C, 58.8; H, 4.2; N, 3.6%); ν_{max}/cm^{-1}: 1670 (asym, CO$_2$) and 1300 (sym, CO$_2$). [Pt(*p*-MeOC$_6$H$_4$)$_2$(OCOPh)$_2$(bpy)]. Yield 83%; mp 104 °C (decomp.) (Found: C, 56.3; H, 3.5; N, 3.7. C$_{38}$H$_{32}$N$_2$O$_6$Pt requires C, 56.5; H, 4.0; N, 3.5%); ν_{max}/cm^{-1}: 1645 (asym, CO$_2$) and 1275 (sym, CO$_2$). [Pt(*p*-MeOC$_6$H$_4$)$_2$(OCOPh)$_2$(phen)]. Yield 80%; mp 101–103 °C (decomp.) (Found: C, 57.5; H, 4.2; N, 3.4. C$_{40}$H$_{32}$N$_2$O$_6$Pt requires C, 57.8; H, 3.8; N, 3.4%); ν_{max}/cm^{-1}: 1650 (asym, CO$_2$) and 1280 (sym, CO$_2$).

Kinetic studies of the reaction of [PtAr$_2$(bpy)] with dibenzoyl peroxide

In a typical experiment, a solution of [Pt(*p*-MeC$_6$H$_4$)$_2$(bpy)] in acetone or benzene (3 ml, 3×10^{-4}M) in a cuvette was thermostated at 20 °C and a known excess of dibenzoyl peroxide was added using a microsyringe. After rapid stirring, the absorbance at $\lambda = 484$ nm (in benzene) or $\lambda = 447$ nm (in acetone) was monitored with time and a plot of $-\ln((A_t - A_\infty)/(A_0 - A_\infty))$ *versus* time gave a good straight line (Fig. 2) from which the observed first-order rate constants and standard deviations were obtained. A plot of k_{obs} *versus* [dibenzoyl peroxide] was

linear (Fig. 3), and the slope gave the second-order rate constant. The same method was used at other temperatures, and activation parameters were obtained from the Arrhenius equation. A similar procedure was used to obtain the rate constants and activation parameters for reaction of dibenzoyl peroxide with other [$PtAr_2$(NN)] complexes at the corresponding λ_{max} values.

A similar procedure was carried out for the reaction of [$PtAr_2$(NN)] (at the corresponding λ_{max}) with H_2O_2 in acetone (or a 2 : 1 mixture of acetone–benzene). The concentration of H_2O_2 was determined by standard method as 9.07 M.

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