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Oxidative Addition of Phthaloyl Peroxide to Dimethylplatinum(II) Complexes

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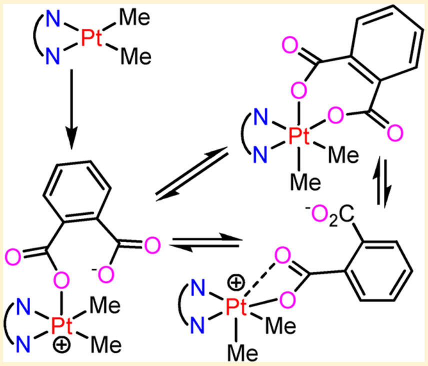
S *Supporting Information*

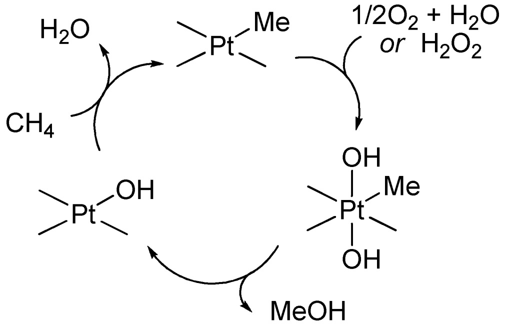
ABSTRACT: Complexes $[PtMe_2(NN)]$, with NN = 2,2′-bipyridine (bipy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu_2bipy), di-2-pyridylamine (dpa), or di-2-pyridyl ketone (dpk), react easily with phthaloyl peroxide to give a mixture of the chelate complex $[PtMe_2\{\kappa^2\text{-}O,O'\text{-}1,2\text{-}(O_2C)_2C_6H_4\}(NN)]$, which was structurally characterized when NN = bu_2bipy, and an oligomer or polymer $[PtMe_2\{\mu\text{-}\kappa^2\text{-}O,O'\text{-}1,2\text{-}(O_2C)_2C_6H_4\}\text{-}(NN)]_n$. In the case with NN = dpa, no phthalate chelate complex is formed. These complexes are easily hydrolyzed, and the complexes *cis*-$[PtMe_2(OH)\{\kappa^1\text{-}O\text{-}O_2CC_6H_4\text{-}2\text{-}CO_2H\}(bipy)]$ and *trans*-$[PtMe_2\{\kappa^1\text{-}O\text{-}O_2CC_6H_4\text{-}2\text{-}CO_2H\}(dpkOH)]$ have been structurally characterized. It is argued that the oxidative addition of phthaloyl peroxide occurs by a polar mechanism and that the hydrolysis is easy because there is no special stability associated with the seven-membered platinum-phthalate chelate ring.



INTRODUCTION

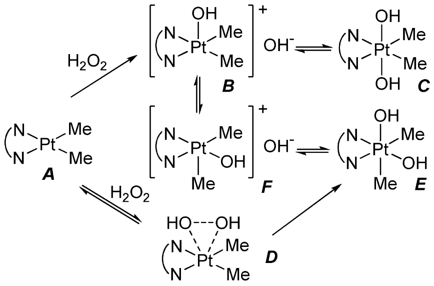
The oxidation of methylplatinum(II) complexes with dioxygen or hydrogen peroxide can give methyl(hydroxo)platinum(IV) complexes,[1] which may then reductively eliminate methanol.[1,2] If the methylplatinum(II) complex can be regenerated by C−H bond activation of methane, a cycle for oxidation of methane to methanol can be envisaged (Scheme 1).[1−3] There are many problems to be overcome if this potential is to be realized, and a deeper understanding of the individual steps is needed.

Scheme 1. Potential Catalysis of Oxidation of Methane to Methanol



The oxidative addition of hydrogen peroxide to dimethylplatinum(II) complexes, ***A***, might occur by a polar stepwise mechanism or a concerted nonpolar mechanism (Scheme 2). In principle, the mechanisms could be distinguished by the stereochemistry of the product, with the polar mechanism leading to the product of *trans* addition, ***C***, by way of the ionic intermediate ***B*** and the concerted mechanism leading to the product of *cis* addition, ***E***, by way of the intermediate ***D***. However, it is possible that the product of *cis* oxidative addition, ***E***, could isomerize rapidly to ***C*** via intermediate ***F***[1e] or that the five-coordinate ionic intermediate ***B*** formed in the polar mechanism could isomerize to ***F*** before hydroxide coordination.[4] The product of *trans* oxidative addition is usually observed,[1] although there are examples of *cis* addition.[1g,2d] Free radical mechanisms might also be considered, although there is no evidence for them.

Scheme 2. Possible Polar and Concerted Mechanisms of Oxidative Addition of Hydrogen Peroxide[a]



[a]NN = diimine ligand.

The oxidative addition of dibenzoyl peroxide can be considered in a similar way. A simple polar mechanism would give the product of *trans* oxidative addition, ***H***, via intermediate ***G***. An ionic intermediate might be stabilized because the $PhCO_2$ group could act as a three-electron ligand by coordination of the carbonyl group in ***K***, and this could give a route to the product of *cis* oxidative addition, ***I***.[1p,5] The

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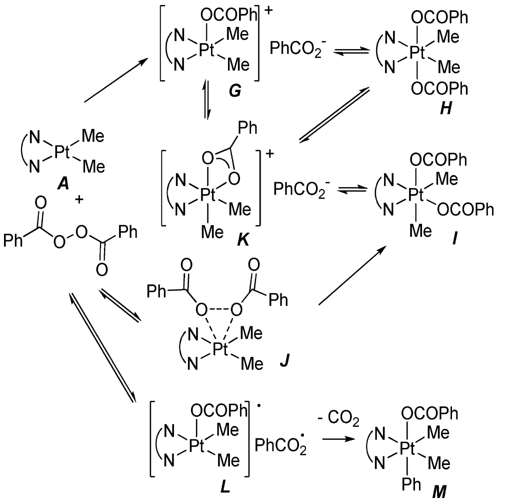
concerted mechanism would give *I* via intermediate *J*, but this could be followed by isomerization to *H* (Scheme 3). The reaction often gives a mixture of the products of *cis* and *trans* oxidative addition, *I* and *H* (Scheme 3).[1e,m,p,5] Only one kinetic study has been reported.[1e] The reaction with [PtPh$_2$(bipy)], bipy = 2,2′-bipyridine, followed second-order kinetics. It gave a large negative value of the entropy of activation, normally indicative of a polar S_N2 mechanism, but the rate showed only a small dependency on the solvent polarity, indicative of a nonpolar mechanism.[6] The authors proposed the concerted mechanism of oxidative addition.[1e] A free radical mechanism involving *L* and intermediate PhCO$_2$· radicals might be expected to give the phenylplatinum complex *M* by decarboxylation of this PhCO$_2$· radical before coordination,[7] but no such products have been observed.[1,5]

Scheme 3. Possible Mechanisms and Products of Oxidative Addition of Dibenzoyl Peroxide



This paper reports the first study of the reactivity of a cyclic acyl peroxide with dimethylplatinum(II) complexes. The high reactivity of phthaloyl peroxide has been recognized and is attributed in part to the nearly eclipsed conformation about the peroxide, with dihedral angle C−O−O−C = 11°.[8−10] In many stoichiometric organic oxidation reactions, phthaloyl peroxide is thought to react by free radical or single-electron-transfer mechanisms,[8−10] and it has recently been studied as an organocatalyst for dihydroxylation of alkenes.[11] It was anticipated that the polar mechanism would give intermediate *N*, which could give either oligomers *P* with *trans*-PtO$_2$ linkages (a trimer is the smallest possible oligomer of this type) or the product of *cis* oxidative addition, *O* (Scheme 4). The concerted mechanism would also give *O* via intermediate *Q*. A free radical mechanism via intermediate *R* might also give *O*, or the intermediate might undergo decarboxylation to give the arylplatinum complex *S*, whose five-membered chelate ring is likely to be stabilized compared to the seven-membered chelate ring of *O*. In fact, the chemistry proved to be complicated by easy hydrolysis of the phthalate complexes.

Scheme 4. Possible Mechanisms and Products of Oxidative Addition of Phthaloyl Peroxide

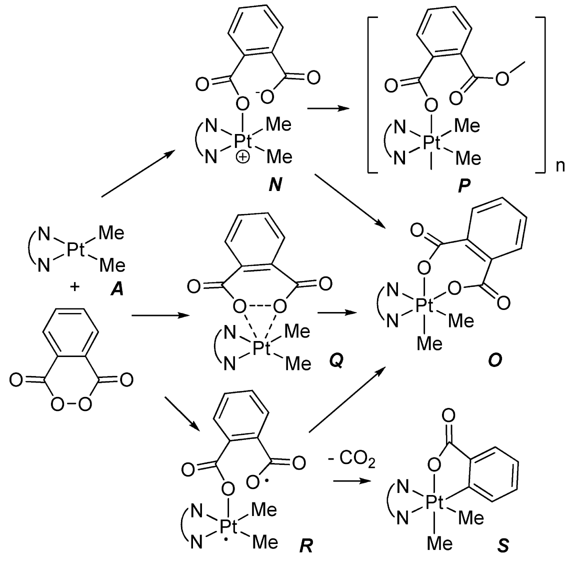
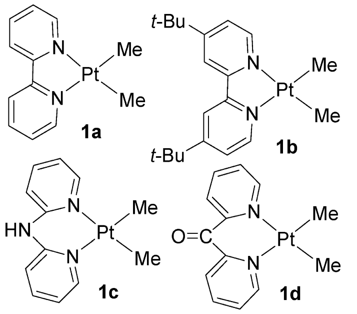


Chart 1. Dimethylplatinum(II) Reagents

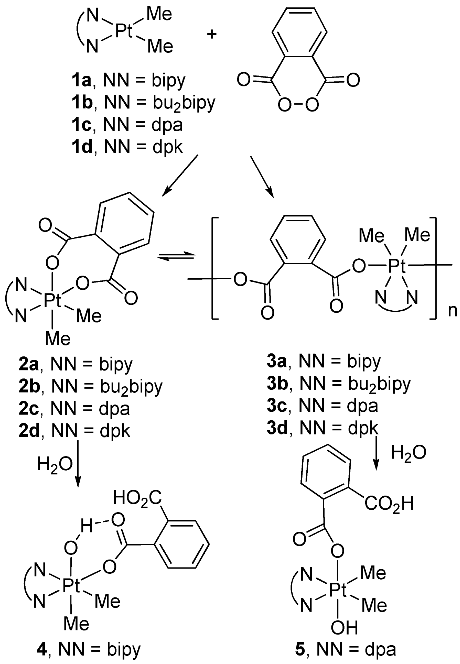


■ RESULTS AND DISCUSSION

Synthesis and Characterization. The reactions of phthaloyl peroxide with the dimethylplatinum(II) complexes shown in Chart 1 were studied. The ligands 2,2′-bipyridine (bipy) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu$_2$bipy) in **1a** and **1b** give five-membered chelate rings, while di-2-pyridylamine (dpa) or di-2-pyridyl ketone (dpk) in **1c** and **1d** give six-membered chelate rings on coordination to platinum.

Phthaloyl peroxide reacted rapidly with all of the complexes [PtMe$_2$(NN)], **1a**−**1d**, according to Scheme 5. For example, an orange solution of [PtMe$_2$(bipy)], **1a**,[12] in acetone-d_6 was immediately decolorized on addition of phthaloyl peroxide. The stereochemistry at platinum in the products **2a** and **3a** was readily deduced from the ^{1}H NMR spectrum. Thus, the product **3a** of *trans* oxidative addition has C_s or C_{2v} symmetry, with a plane of symmetry bisecting the Me$_2$Pt group, so the ^{1}H NMR spectrum contains a single methylplatinum resonance and four resonances for the bipy protons, whereas the product **2a** of *cis* oxidative addition has only C_1 symmetry, so the ^{1}H NMR spectrum contains two methylplatinum resonances and eight resonances for the bipy protons. In this case, a mixture of **2a** [δ(MePt) 1.09, ^2J(PtH) 69 Hz; δ(MePt) 1.15, ^2J(PtH) 71 Hz] and **3a** [δ(MePt) 1.88, ^2J(PtH) 70 Hz] was formed. The ESI-MS in acetone solution contained a major envelope of peaks centered at m/z = 546.1, corresponding to [**2a** + H]$^+$, and a lower intensity peak at m/z = 1091.2, which corresponds to [{PtMe$_2$(phthalate)(bipy)}$_2$ + H]$^+$ and might be assigned to **3a**, with n = 2 (but note that one of the platinum(IV) centers would be five-coordinate). The highest mass peak observed was at m/z = 1450, which corresponds to [**3a** (n = 3) − bipy − 2Me + H]$^+$, indicating that oligomers with at least n = 3 are present.

Scheme 5. Formation of Phthalate Complexes by Oxidative Addition[a]



[a] Complexes **3** were identified by NMR spectroscopy, and **2c** was not detected (see text).

Table 1 lists the ratio of the products **3a**/**2a** as a function of solvent and reaction time for reactions carried out in a sealed NMR tube. It can be seen that in the polar solvent CD_3OD essentially equal amounts of **3a** and **2a** were formed and that the product ratio did not change over the course of a week at room temperature. In the least polar solvent CD_2Cl_2, the initial ratio of **3a**/**2a** was 1.5, but this ratio increased slowly but dramatically to 25 in a week. The mixture in acetone-d_6 gave an intermediate degree of isomerization over time (Table 1).

Table 1. Ratio of Products 3a/2a As a Function of Solvent and Reaction Time

solvent	5 min	1 day	7 days
CD_3OD	1.0	1.0	1.0
$(CD_3)_2CO$	1.6	3.5	4.1
CD_2Cl_2	1.5	5.7	25

The product ratio was strongly dependent on the diimine ligand. Thus, for reaction in dry acetone-d_6 solution, the initial product ratio for NN = bipy was **3a**/**2a** = 1.6, but, for the similar ligand NN = bu_2bipy, it was **3b**/**2b** = 0.12. For NN = dpa, only the *trans* adduct **3c** was detected. For NN = dpk, the isomer ratio could not be determined by integration of the ^1H NMR spectrum because the *trans* product **3d** was sparingly soluble and partly precipitated from solution.

From these initially formed complexes **2** and **3**, only complex **2b** could be recrystallized successfully, and its structure is shown in Figure 1. The platinum(IV) center has octahedral stereochemistry with the *cis,cis,cis*-$PtO_2N_2C_2$ arrangement of donor groups. The complex is therefore chiral, but it crystallizes as a racemic mixture of ***C*** and ***A*** enantiomers. The high *trans* influence of the methyl groups causes the distances Pt–O(2) and Pt–N(2) to be longer than Pt–O(1) and Pt–N(1), respectively. The chelate bite angle of the phthalate [seven-membered ring, O(1)–Pt–O(2) 92.3(2)°] is naturally greater than for the bu_2bipy ligand [five-membered ring, N(1)–Pt–N(2) 79.3(2)°]. The folded conformation of the PtO_2C_4 ring of the chelating phthalate is achieved by twisting the carboxylate groups out of the plane of the phenylene ring (twist angles for the C(28)O(2)O(4) and C(21)O(1)O(3) groups are 38° and 80°, respectively). The carbonyl distances C(21)–O(3) and C(28)–O(4) are shorter than the C–OPt distances C(21)–O(1) and C(28)–O(2), indicating significant covalent character in the Pt–O bonds. The ESI-MS of **2b** in acetone solution gave the major peak at $m/z = 658.2$, corresponding to $[\mathbf{2b} + H]^+$, with no dimer or trimer peaks. The ^1H NMR and ESI-MS data both indicate that the equilibration of **2b** with its isomer **3b** is slow at room temperature.

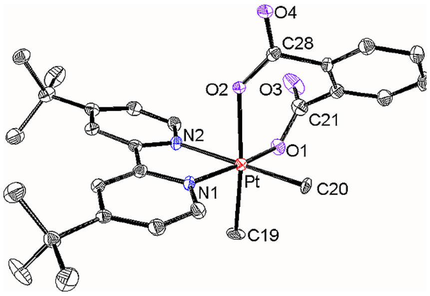


Figure 1. Structure of complex **2b**. Selected bond parameters (Å and deg): Pt–O(1) 2.020(5); Pt–O(2) 2.160(4); Pt–N(1) 2.027(5); Pt–N(2) 2.120(5); Pt–C(19) 2.067(6); Pt–C(20) 2.063(6); O(1)–C(21) 1.296(8); O(3)–C(21) 1.221(9); O(2)–C(28) 1.291(8); O(4)–C(28) 1.223(8); N(1)–Pt–N(2) 79.3(2); O(1)–Pt–O(2) 92.3(2).

The mixture of **2a** and **3a** was difficult to crystallize, but single crystals were finally obtained by the slow diffusion of pentane into a solution in dichloromethane, stored at 5 °C for several weeks. The complex that crystallized was formed by hydrolysis and had the stoichiometry either $[PtMe_2(O_2CC_6H_4CO_2H)(OH)(bipy)]\cdot 4.5H_2O$, **4**, Scheme 5, or $[PtMe_2(O_2CC_6H_4CO_2)(OH_2)(bipy)]\cdot 4.5H_2O$, **4′**, with some uncertainty in the positions of hydrogen atoms. Note that **4** is expected to be the kinetic product of hydrolysis of **2a** because its formation would involve cleavage of the weaker Pt–O bond of **2a** *trans* to the methyl group. There are two independent but similar molecules in the crystal of **4**, and the structure of a pair of Pt(1) molecules, connected by hydrogen-bonded water molecules, is shown in Figure 2. As in complex **2b**, the platinum(IV) centers have octahedral stereochemistry with the *cis,cis,cis*-$PtO_2N_2C_2$ arrangement of donor groups, but in complex **4** the phthalate groups act as monodentate ligands, and there is a coordinated hydroxide (**4**) or water (**4′**) group as the second oxygen-donor ligand. The two molecules in Figure 2 are related by an inversion center, so they represent a racemic pair and are connected through hydrogen bonds to the water molecules O(9S) and O(9SA), as well as being involved in hydrogen bonding to several other water molecules. The hydrogen atoms could not be located directly, so the nature of the hydrogen bonding is not obvious. Based on OO distances, hydrogen bonds are present between the atoms O(2)···O(5) = 2.60(2), O(5)···O(9S) = 2.64(2), and O(4)···O(9SA) = 2.82(2) Å, as well as O(3)···O(7S) = 2.70(2) and O(4)···O(5S) = 2.70(2) Å. Another clue is that the carbon–oxygen distances of the C(11)O(1)O(2) carboxyl group are consistent with the presence of a single and double bond [C(11)–O(1) = 1.32(1) Å, C(11)–O(2) = 1.24(2) Å] but that

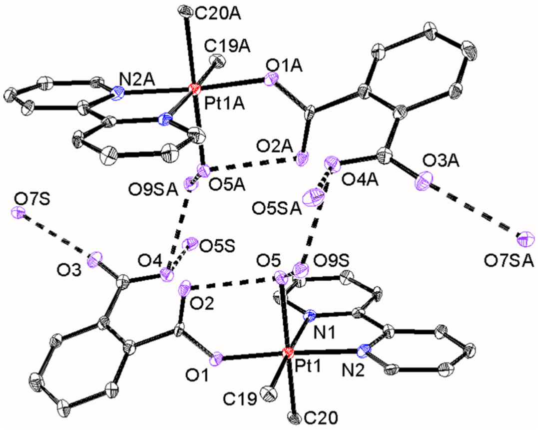
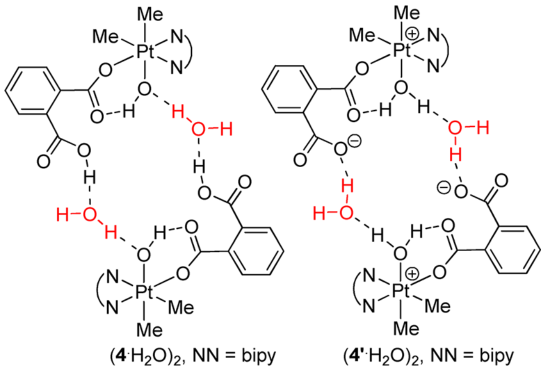


Figure 2. Structure of a racemic pair of molecules of complex **4**, with connecting water molecules. Selected bond parameters (Å): Pt(1)−O(1) 2.013(9); Pt(1)−O(5) 2.206(9); Pt(1)−N(1) 2.10(1); Pt(1)−N(2) 2.01(1); Pt(1)−C(19) 2.04(1); Pt(1)−C(20) 2.06(1); O(1)−C(11) 1.32(1); O(2)−C(11) 1.24(2); O(3)−C(18) 1.24(2); O(4)−C(18) 1.25(2). Symmetry equivalent A: 2−*x*, 1−*y*, −*z*.

Chart 2. Hydrogen Bonding and Structures of 4 and 4′



the carbon−oxygen distances of the C(18)O(3)O(4) carboxyl group are equal within experimental error [C(18)−O(3) = 1.24(2) Å, C(18)−O(4) = 1.25(2) Å], suggesting the presence of a carboxylate anion. Chart 2 indicates that only a small motion of hydrogen atoms is needed to interconvert the structures **4** and **4′**, and so there is no easy way to determine which of them is the dominant form in the crystalline state. In complexes $[Pt(OH)(OH_2)Me_2(NN)]^+$, it has been shown that the acidity of the aqua group is similar to that of a carboxylic acid,[1c] so **4** and **4′** are likely to have similar stability provided that they can form the same number and strength of intermolecular and intramolecular hydrogen bonds.

Figure 3 shows a section of the complex hydrogen-bonded network structure formed by self-assembly of complex **4** and the nine independent water molecules. Racemic pairs of Pt(1) and Pt(2) molecules are connected through hydrogen bonding to O(9S) and O(8S), respectively, and Pt(1) and Pt(2) molecules are connected by hydrogen bonding of the uncoordinated carboxylic acid/carboxylate groups to O(7S). There are also longer range connections of the complexes through chains of bridging water molecules (Figure 3).

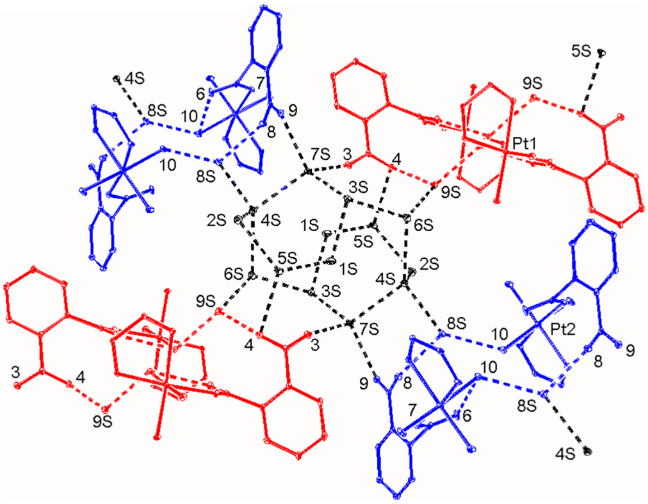
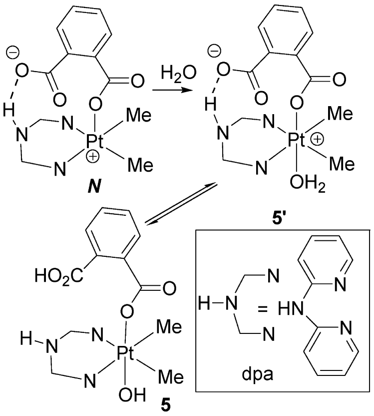


Figure 3. Part of the hydrogen-bonding network in complex **4**. Pt(1) and Pt(2) molecules, and the connecting water molecules O(9S) and O(8S), are shown in red and blue, respectively, and only the NCCN atoms of the bipy groups are shown, for clarity. Only the numeric labels of the O-atoms are given, with S indicating a water molecule [e.g., 3 = O(3), 1S = O(1S)].

Scheme 6. Possible Structures of Intermediate *N* and Product 5 or 5′[a]

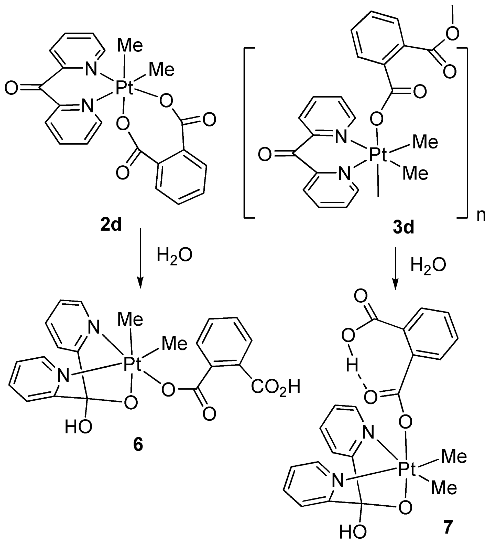


[a] Only the $HN(CN)_2$ backbone atoms of the dpa ligand (inset) are shown, for clarity.

Complex **5** was sparingly soluble and did not give single crystals, so its proposed structure is based on spectroscopic studies only. The ^1H NMR spectrum contains a single methyl platinum resonance at $\delta = 1.61$, with coupling $^2J(PtH) = 67$ Hz, and only four pyridyl resonances and two phthaloyl resonances, clearly indicating that it has at least C_s symmetry, as expected for a product of *trans* oxidative addition. The complex with dpa is the only one studied that gives no detectable amount of a *cis* product. We tentatively suggest that this could be because, in the polar intermediate ***N*** (Scheme 6), the free carboxylate group can hydrogen bond to the NH proton of dpa. Molecular modeling indicates that this hydrogen bond cannot be formed by a *cis* isomer, and the effect may be strong enough to prevent rearrangement of ***N*** to form the chelating phthalate group. The isolated complex analyzed as $[PtMe_2(phthalate)(OH_2)(dpa)]$, consistent with either structure **5** or **5′** (Scheme 6). The ESI-MS in acetone did not give a parent ion but contained prominent peaks centered at m/z = 413.1 and 561.1, corresponding to $[\mathbf{5}\text{-phthalate-H}]^+$ and $[\mathbf{5}\text{-OH}]^+$, respectively. The peak at m/z = 413.1 supports the presence of a coordinated hydroxide or water molecule, but the data do not clearly distinguish between the two possible structures **5** and **5′**. As in complex **4**, it is likely that there is extensive intermolecular hydrogen bonding in the solid state, and this may rationalize the low solubility of the complex.

The red complex [$PtMe_2$(dpk)], **1d**, reacted rapidly with phthaloyl peroxide. The initial products are thought to be **2d** and **3d** (Scheme 5), but, following purification, the two colorless complexes **6** and **7**, which are formed by hydration, were isolated (Scheme 7). These complexes could be separated because complex **7** was sparingly soluble and precipitated from solution in moist acetone. Complexes **6** and **7** can be considered as derivatives of the products of *cis* and *trans* oxidative addition, **2d** and **3d**, respectively (Scheme 7). Once formed, the complexes did not easily interconvert. The overall stereochemistry at platinum(IV) was readily determined from the ^{1}H NMR spectra. Thus, complex **6** gave two equal intensity methylplatinum resonances at δ = 1.94 and 2.04, each with ^2J(PtH) = 70 Hz, while **7** gave a single methylplatinum resonance at δ = 1.64, with ^2J(PtH) = 70 Hz.

Scheme 7. Formation and Structures of Complexes 6 and 7



Complex **6** has not given good single crystals, but complex **7** could be crystallized and its structure is shown in Figure 4. The platinum(IV) center has octahedral stereochemistry with the *trans,cis,cis*-$PtO_2N_2C_2$ arrangement of donor atoms, corresponding to *trans* oxidative addition. The phthalate is present in the monoprotonated form, and there is a strong intramolecular hydrogen bond to an oxygen atom of the coordinated carboxylate group, with O(4)⋯O(3) = 2.46(1) Å. The dpk ligand has been converted to the ketal derivative dpkOH$^-$, which is bound as a *fac*-tridentate ligand. This derivatization of the dpk ligand has been observed previously, for example in the oxidative addition of hydrogen peroxide to complex **1d**, and may involve hydroxide attack on the carbonyl group of dpk.[1n,2d] The dimer shown in Figure 4 is formed by self-assembly through complementary hydrogen bonding between the C(OH)(OPt) units of neighboring molecules, with O(6)⋯O(1A) = O(1)⋯O(6A) = 2.70(1) Å.

Complex **6** is structurally characterized only by elemental analysis, which indicates the presence of a molecule of water, and by spectroscopic methods. The ^{1}H NMR spectrum indicates the *cis,cis,cis* stereochemistry of the $PtO_2N_2C_2$ donors (Figure S1). The carbonyl group of the coordinated dpk ligand in complex **1d** gives a strong peak at 1682 cm^{-1} in the IR spectrum, but complex **6** gives only carbonyl stretches in the range 1650−1605 cm^{-1}, characteristic of the phthalate group. This observation indicates that complex **6** contains the dpkOH$^-$ ligand rather than the original dpk ligand. The ESI-MS, in the presence of NaI to aid ionization, gave a peak at *m/z* = 614.1, which is assigned to the ion [$Pt(C_8H_5O_4)Me_2(dpkOH)Na]^+$. Together, these data strongly support the proposed structure of complex **6**. The complex is expected to self-associate through intermolecular hydrogen bonding in the solid state, but we have no data to determine how this occurs.

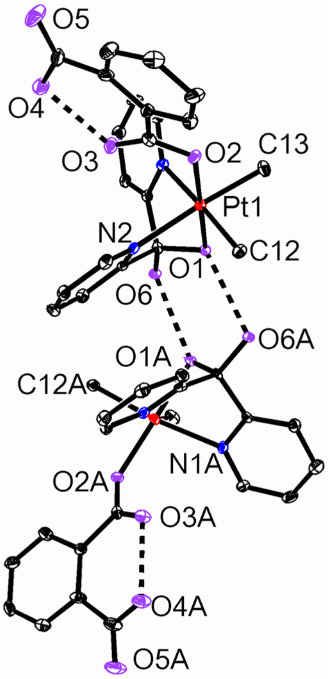


Figure 4. Structure of complex **7**, showing the dimer formed by intermolecular hydrogen bonding. Selected parameters: Pt(1)−N(1) 2.146(8); Pt(1)−N(2) 2.153(9); Pt(1)−O(1) 2.009(6); Pt(1)−O(2) 2.046(7); Pt(1)−C(12) 2.06(1); Pt(1)−C(13) 2.03(1); O(1)−C(6) 1.438(7); O(2)−C(14) 1.30(1); O(3)−C(14) 1.23(1); O(4)−C(21) 1.31(1); O(5)−C(21) 1.20(1) Å. Symmetry equivalent A: 1−*x*, *y*, −1/2−*z*.

Computational Studies. The synthetic and structural study has given insight into the mechanism of reaction of the dimethylplatinum(II) complexes with phthaloyl peroxide, PP, but several puzzles remain. These were addressed by computational studies using DFT. Scheme 4 outlines the potential polar, concerted, or radical mechanisms, which involve intermediates (or transition states) ***N***, ***Q***, or ***R***, respectively. The polar mechanism with **1a** involves end-on attack with the 5d$_{z^2}$ orbital of platinum (HOMO) as nucleophile and the σ*(OO) orbital of PP (LUMO) as acceptor, as shown in Figure 5a, leading to cleavage of the O−O bond and formation of the zwitterionic intermediate ***N***. This is calculated to be energetically favorable (Figure 6) with a low activation energy. This polar mechanism has previously been supported for oxidative addition of halogens, many peroxides, and alkyl halides.[1,6,13] The radical mechanism is expected give an intermediate ***R*** with similar structure to ***N***, but the calculation does not support this mechanism since spin-paired structures are found to be more stable. The concerted mechanism is expected to involve side-on approach with transfer of electrons from a 5d$_\pi$ orbital (HOMO−1) of **1a** to the σ*(OO) orbital of PP, as shown in

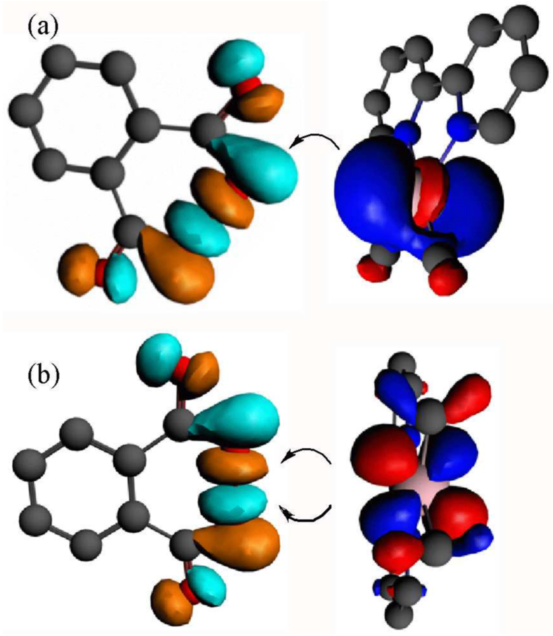


Figure 5. Frontier orbitals for (a) polar mechanism and (b) concerted mechanism of reaction of phthaloyl peroxide with **1a**.

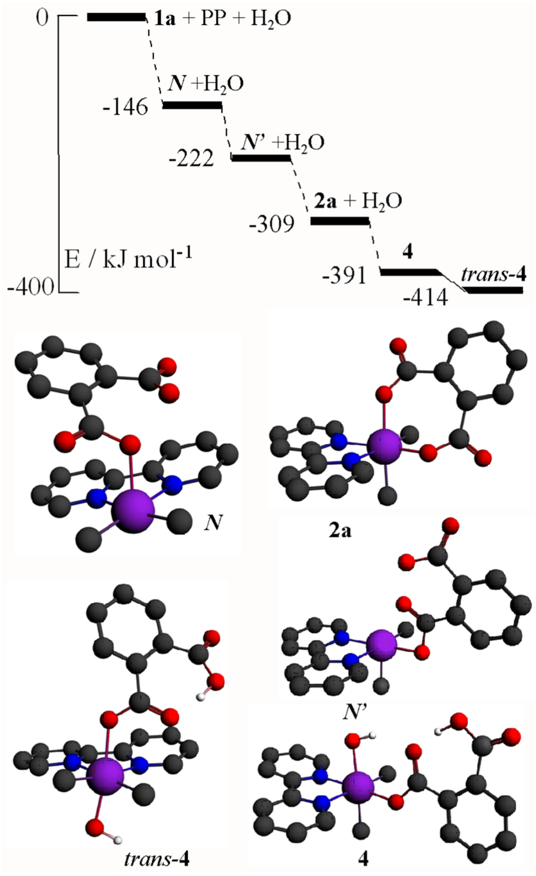


Figure 6. (Above) Calculated relative energies (kJ mol^{-1}) and (below) calculated structures for intermediates and products of the reaction of phthaloyl peroxide (PP) with complex **1a**.

Figure 5b. This mechanism would lead directly to complex **2a**, but no easy route could be found. There are difficulties because the rigid planar structure of **1a** must distort to allow formation of two new bonds in **2a** and because the side-on approach leads to strong repulsion between the filled $2p_\pi$ orbitals of PP and the filled 5d orbitals of **1a**. Concerted oxidative addition to platinum(II), or reductive elimination from platinum(IV), usually occurs after dissociation of a ligand to make a coordinatively unsaturated reagent, but this is difficult for **1a**. The present theory supports this pattern of behavior and predicts easy reaction through the polar mechanism.[1−6,14]

Figure 6 shows that the rearrangement of the intermediate ***N*** to give **2a** is calculated to be favorable. This could occur directly or via its isomer ***N***′ (Figure 6). In ***N***′, the coordinative unsaturation at platinum is relieved by semichelation by a single carboxylate group (calculated Pt−O = 2.05, Pt···O 2.39 Å), and it lies about midway in energy between ***N*** and **2a**. The hydrolysis of **2a** to give **4** is also favored. The gas phase calculation indicates that the hydroxo form **4** is more stable than the aqua complex isomer, but the calculated and experimental structures differ (Figure 2, Chart 2), because there is intermolecular hydrogen bonding to water in the structure determined experimentally. Figure 6 also indicates that the *trans* isomer, labeled *trans*-**4**, is calculated to be more stable than **4**. Results from similar calculations for the reactions of the dpa complex **1c** are shown in Figure 7. The relative energies are similar to those for compounds formed from **1a** (Figure 6), but the reaction of **1c** did not give detectable amounts of either **2c** or *cis*-**5** as products. The intermediate ***N*** is calculated to have a hydrogen bond between the carboxylate and NH groups (Figure 7), and so the calculation lends support

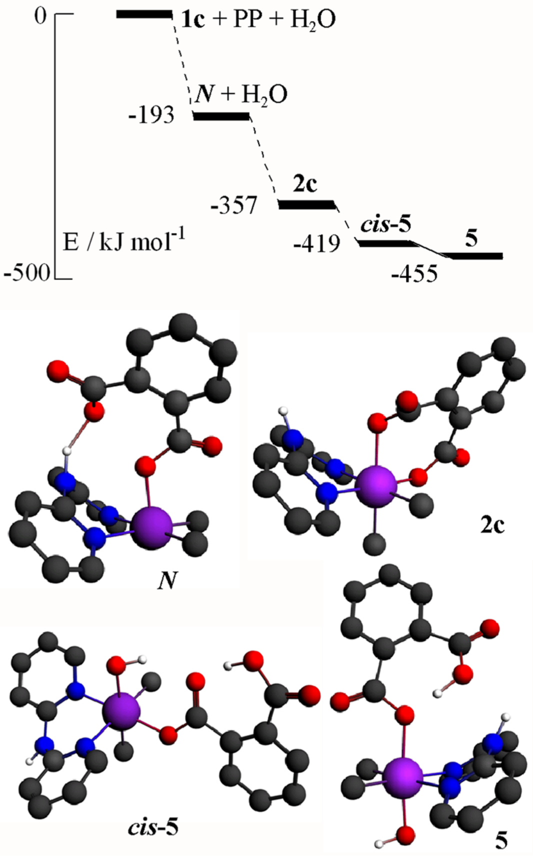
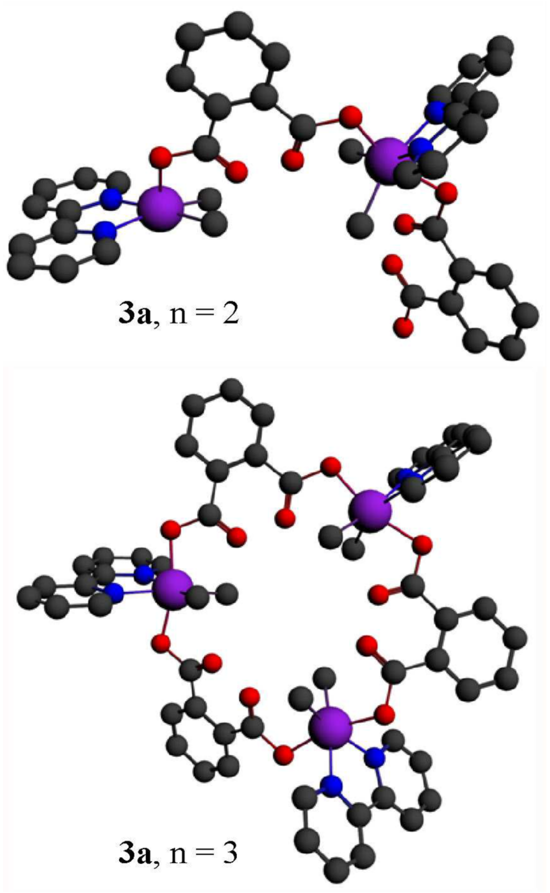


Figure 7. (Above) Calculated relative energies (kJ mol^{-1}) and (below) calculated structures for intermediates and products of the reaction of phthaloyl peroxide (PP) with complex **1c**.

to the hypothesis (Scheme 6) that rearrangement to **2c** is slower than either oligomerization to give **3c** or addition of water to give **5** (Figure 7). There seems to be no thermodynamic reason that **2c** could not be formed.

The structure of the proposed oligomeric compounds **3** (Scheme 5) remains undetermined. Figure 8 shows calculated models for a dimer or trimer for **3a**. It can be seen that the dimer (and higher linear oligomers) must contain a five-coordinate platinum(IV) center and a free carboxylate group. The coordinative unsaturation at platinum(IV) might be relieved by solvent coordination, but these structures would contain nonequivalent platinum(IV) centers and so would be expected to have more complex ^{1}H NMR spectra than those observed. A cyclic trimer is the smallest oligomer that might contain equivalent platinum(IV) centers (Figure 8).



3a, n = 2

3a, n = 3

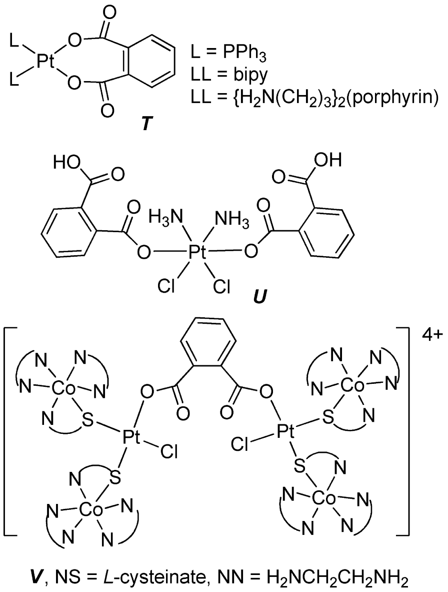
Figure 8. Possible structures for complex **3a**: (above) a dimer containing a coordinatively unsaturated platinum(IV) center and an uncoordinated carboxylate group; (below) the cyclic trimer.

■ CONCLUSIONS

The combination of experimental and computational studies of the oxidative addition reactions of complexes **1a**–**1d** with phthaloyl peroxide supports the polar mechanism of reaction, in which the zwitterionic complex ***N*** (Scheme 4) is the key intermediate. This intermediate can rearrange to give the chelate complexes **2a**–**2d** or oligomerize to give the bridging phthalate complexes **3a**–**3d**. Further slow isomerization of **2a** to **3a** has been observed in solution (Table 1). The equilibria and rates of equilibration are strongly dependent on both the nature of the supporting diimine ligand and the solvent. The concerted mechanism of reaction through intermediate ***O*** (Scheme 4) would be expected to give the chelating phthalate complex more selectively, while the radical mechanism through intermediate ***R*** might be expected to give products of rearrangement or decarboxylation, such as ***S*** (Scheme 4).

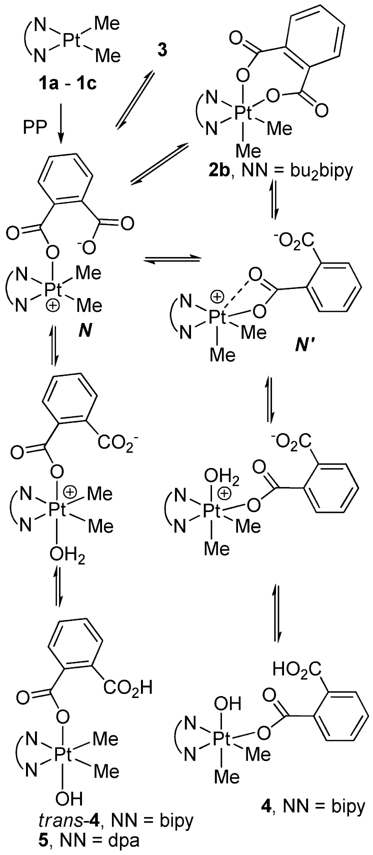
A survey of known phthalate coordination complexes, published in 2004, identified no less than 26 different bonding modes of the phthalate group.[15] The chelate structure established for complex **2b** is relatively uncommon and is established mostly with small metal ions such as Be^{2+} and Ti^{4+}.[16] Complex **2b** appears to be the first crystallographically characterized example of a platinum complex with chelating phthalate (Figure 1). The chelate structure has previously been suggested, based on spectroscopic characterization, for several platinum(II) complexes (***T***, Chart 3) but not for platinum(IV) complexes.[17] The monodentate structure, established for complexes **4** and **7** (Figures 2 and 4), is also unusual,[15] but it has previously been established in the platinum(IV) complex ***U*** (Chart 3).[18] The bridging structure, suggested here for complexes **3a**–**3d** (Scheme 5), is much more common[15] and has been established for one platinum(II) complex, ***V*** (Chart 3).[19] An unspecified bridging mode has also been suggested for phthalate "platinum blues".[20] Clearly there is no special stability associated with the seven-membered ring formed by the chelating phthalate group.

Chart 3. Some Known Platinum Phthalate Complexes



The overall proposed mechanisms of formation of some of the characterized complexes is shown in Scheme 8 and will be discussed for the case with NN = bipy. The primary intermediate is thought to be ***N***, which can react rapidly to give the oligomer **3a**, with bridging phthalate groups, or the monomeric complex **2a**, with chelating phthalate groups. The easy isomerization of ***N*** to its isomer ***N′*** may precede formation of **2a**. The ratio of the initially formed products **2a** and **3a** is dependent on these fast reactions (Table 1). Once formed, complexes **2** and **3** can equilibrate more slowly by dissociation of one of the Pt–O bonds to re-form ***N*** or ***N′*** (Scheme 8). The hydrolysis reactions to give **4** or *trans*-**4** must also involve the intermediates ***N*** and/or ***N′***. Once formed, these complexes

Scheme 8. Proposed Mechanisms for Formation of the Isolated Complexes 2, 4, and 5



equilibrate only slowly. The surprisingly complex chemistry can therefore be rationalized in terms of Scheme 8.

■ EXPERIMENTAL SECTION

Reactions were carried out using standard Schlenk techniques, unless otherwise stated. NMR spectra were recorded using a Varian Mercury 400 or Varian INOVA 400 or 600 MHz spectrometer. ^{1}H NMR chemical shifts are reported relative to TMS. Mass spectrometric analysis was carried out using an electrospray PE-Sciex mass spectrometer (ESI-MS) coupled with a TOF detector.

The complexes [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] and **1a**−**1d** were prepared according to the literature.[1n,12,21] Phthaloyl peroxide was prepared by the method of Russell and recrystallized twice from benzene/pentane until pure by NMR.[9] NMR in CDCl$_3$: δ(^{1}H) 8.04 (m, 2H, H^{3}); 8.30 (m, 2H, H^{2}). ESI-MS: *m*/*z* 165.03, calcd for $[C_8H_4O_4+H]^+$ *m*/*z* 165.01.

DFT calculations were carried out by using the Amsterdam Density Functional program based on the BLYP functional, with double-ζ basis set and first-order scalar relativistic corrections.[22] The reported results are from gas phase calculations. The energy minima were confirmed by vibrational frequency analysis in each case.

Monitoring by ^{1}H NMR Spectroscopy. In a typical experiment, phthaloyl peroxide (1.6 mg, 0.01 mmol) was added to a solution of **1a** (3.8 mg, 0.01 mmol) in acetone-*d*$_6$ (1 mL) in an NMR tube. The tube was sealed, and spectra were recorded at intervals over a period of 1 week. The reaction gave a mixture of **2a** and **3a**. NMR in acetone-*d*$_6$, **2a**: δ(^{1}H) 1.09 (s, 3H, ^{2}J(PtH) = 69 Hz, MePt), 1.15 (s, 3H, ^{2}J(PtH) = 71 Hz, MePt). **3a**: δ(^{1}H) 1.88 (s, 6H, ^{2}J(PtH) = 70 Hz, MePt), 7.30−9.25 [m, bipy, phthalate]. Integration of the methylplatinum resonances gave the ratio of **2a**:**3a** (Table 1). Similarly were identified, from complex **1b**: **2b**, δ(^{1}H) 1.01 (s, 3H, ^{2}J(PtH) = 68 Hz, PtMe), 1.10 (s, 3H, ^{2}J(PtH) = 70 Hz, Pt-Me); **3b**, δ(^{1}H) 1.87 (s, 6H, ^{2}J(PtH) = 71 Hz, PtMe); from complex **1c**: **3c**, δ(^{1}H) 1.82 (s, 6H, ^{2}J(PtH) = 66 Hz, PtMe); from complex **1d**: **3d**, δ(^{1}H) 1.71 (s, 6H, ^{2}J(PtH) = 69 Hz, PtMe).

[PtMe$_2$(bu$_2$bpy)(C$_8$H$_4$O$_4$)], 2b. Phthaloyl peroxide (6.0 mg, 0.0405 mmol) was added to a solution of [PtMe$_2$(bu$_2$bpy)] (20.0 mg, 0.0405 mmol) in acetone (5 mL). The color changed immediately from orange to colorless. The product was precipitated by addition of pentane, then separated and washed with pentane (3 × 2 mL) and ether (3 × 2 mL) and dried *in vacuo*. It was recrystallized from CH$_2$Cl$_2$/pentane by slow diffusion. NMR in acetone-*d*$_6$: δ(^{1}H) 1.01 (s, 3H, ^{2}J(PtH) = 68 Hz, PtMe *trans* to N), 1.10 (s, 3H, ^{2}J(PtH) = 70 Hz, Pt-Me *trans* to O), 1.40 (s, 9H, *t*-Bu), 1.44 (s, 9H, *t*-Bu), 7.30−7.70 (m, 4H, phth), 7.73 (dd, 1H, ^{3}J(H$^{5'}$H$^{6'}$) = 6 Hz, ^{4}J(H$^{5'}$H$^{3'}$) = 1 Hz, H$^{5'}$), 8.01 (dd, 1H, ^{3}J(H^{5}H^{6}) = 6 Hz, ^{4}J(H^{5}H^{3}) = 1 Hz, H^{5}), 8.50 (d, 1H, ^{3}J(H^{5}H^{6} = 6 Hz, ^{3}J(PtH^{6}) = 22 Hz, H^{6}), 9.06 (d, 1H, ^{3}J(H$^{5'}$H$^{6'}$) = 6 Hz, H$^{6'}$), 9.08 (d, 1H, ^{4}J(H^{3}H^{5}) = 1 Hz, H^{3}), 9.12 (d, 1H, ^{4}J(H$^{3'}$H$^{5'}$) = 1 Hz, H$^{3'}$). ESI-MS: *m*/*z* 658.2; calcd for [**2b**+H]$^{+}$, 658.22. Anal. Calcd for $C_{28}H_{34}N_2O_4Pt{\cdot}CH_2Cl_2$: C, 48.89; H, 5.04; N, 4.00. Found: C, 48.82; H, 4.93; N, 3.61.

[PtMe$_2$(O$_2$CC$_6$H$_4$CO$_2$H)(OH)(bipy)], 4. Phthaloyl peroxide (7.70 mg, 0.0525 mmol) was added to a solution of [PtMe$_2$(bpy)] (20.0 mg, 0.0525 mmol) in acetone (5 mL). The color changed from orange to colorless. Pentane was added to precipitate the product as a white solid, which was separated, washed with pentane (3 × 2 mL) and ether (3 × 2 mL), and then dried *in vacuo*. NMR analysis indicated the presence of both **4** and *trans*-**4**, and recystallization from CH$_2$Cl$_2$/pentane gave **4**·4.5H$_2$O. NMR in acetone-*d*$_6$: *trans*-**4**, δ(^{1}H) 2.20 (s, 6H, ^{2}J(PtH) = 66 Hz, Me), 7.2−7.7 (m, 4H, phth), 7.84 (dd, 2H, ^{3}J(H^{5}H^{6}) = 6 Hz, ^{3}J(H^{4}H^{5}) = 8 Hz, H^{5}), 8.23 (dd, 2H, ^{3}J(H^{4}H^{5}) = 8 Hz, ^{3}J(H^{4}H^{3}) = 7 Hz, H^{4}) 8.60 (d, 2H, ^{3}J(H^{3}H^{4}) = 7 Hz, H^{3}), 9.38 (d, 2H, ^{3}J(H^{6}H^{5}) = 6 Hz, H^{6}). **4**, δ(^{1}H) = 1.10 (s, 3H, ^{2}J(PtH) = 70 Hz, PtMe), 1.15 (s, 3H, ^{2}J(PtH) = 69 Hz, PtMe), 7.2−7.7 (m, 4H, phth), 7.81 (dd, 1H, ^{3}J(H^{5}H^{6}) = 7 Hz, ^{3}J(H^{5}H^{4}) = 8 Hz, H^{5}) 8.05 (dd, 1H, ^{3}J(H$^{5'}$H$^{6'}$) = 6 Hz, ^{3}J(H$^{4'}$H$^{5'}$) = 8 Hz, H$^{5'}$), 8.36 (dd, 1H, ^{3}J(H$^{4'}$H$^{3'}$) = 8 Hz, ^{3}J(H$^{4'}$H$^{5'}$) = 8 Hz, H$^{4'}$), 8.37 (dd, 1H, ^{3}J(H^{3}H^{4}) = 8 Hz, ^{3}J(H^{4}H^{5}) = 8 Hz, H^{4}), 8.73 (d, 1H, ^{3}J(H^{3}H^{4}) = 8 Hz, H^{3}), 8.79 (d, 1H, ^{3}J(H$^{3'}$H$^{4'}$) = 8 Hz, H$^{3'}$), 9.20 (d, 1H, ^{3}J(H$^{6'}$H$^{5'}$) = 6 Hz, H$^{6'}$), 9.39 (d, 1H, ^{3}J(H^{6}H^{5}) = 7 Hz, H^{6}). ESI-MS: *m*/*z* 546.1; calcd for [**4**+H]$^{+}$, 546.10. Anal. Calcd for $C_{20}H_{18}N_2O_4Pt{\cdot}H_2O$: C, 42.63; H, 3.58; N, 4.97. Found: C, 42.36; H, 3.41; N, 4.51.

[PtMe$_2$(O$_2$CC$_6$H$_4$CO$_2$H)(OH)(dpa)], 5. This was prepared in a similar way to **4**, but using [PtMe$_2$(dpa)], **1c**. Yield: 73%. NMR in CD$_3$OD: δ(^{1}H) 1.61 (s, 6H, ^{2}J(PtH) = 67 Hz, PtMe), 7.30 (ddd, 2H, ^{3}J(H^{5}H^{6}) = 6 Hz, ^{3}J(H^{5}H^{4}) = 8 Hz, ^{4}J(H^{5}H^{3}) = 1 Hz, H^{5}), 7.40 (d, 2H, ^{3}J(H^{3}H^{4}) = 8 Hz, H^{3}), 7.58 (m, 2H, phth), 7.99 (ddd, 2H, ^{3}J(H^{4}H^{5}) = 8 Hz, ^{3}J(H^{4}H^{3}) = 8 Hz, ^{4}J(H^{4}H^{6}) = 2 Hz, H^{4}), 8.19 (m, 2H, phth), 8.45 (dd, 2H, ^{3}J(H^{6}H^{5}) = 6 Hz, ^{4}J(H^{6}H^{4}) = 2 Hz, H^{6}). ESI-MS: *m*/*z* = 413.1, 561.1; calcd for [PtMe$_2$(OH)(dpa)]$^{+}$, 413.1; [PtMe$_2$(dpa)(C$_8$H$_5$O$_4$)]$^{+}$, 561.1 g/mol. Anal. Calcd for $C_{20}H_{21}N_3O_5Pt{\cdot}1.5H_2O$: C, 39.67; H, 4.00; N, 6.94. Found: C, 39.71; H, 3.79; N, 6.62.

[PtMe$_2$(O$_2$CC$_6$H$_4$CO$_2$H)(dpkOH)], 6 and 7. To a stirring solution of [PtMe$_2$(dpk)] (126 mg, 0.307 mmol) in acetone was added a solution of phthaloyl peroxide (50 mg, 0.307 mmol) in acetone (5 mL). The initial red color of the solution changed to colorless, and a white precipitate formed after 10 min. The solution was filtered to give **7** as a white solid, which was washed with pentane (3 × 2 mL) and ether (3 × 2 mL) and dried *in vacuo*. Pentane was added to the filtrate to precipitate **6** as a white solid, which was separated and washed as above. *cis*-[PtMe$_2$(O$_2$CC$_6$H$_4$CO$_2$H)(dpkOH)], **6**: NMR in acetone-*d*$_6$: δ(^{1}H) 1.94 (s, 3H, ^{2}J(PtH) = 70 Hz, PtMe), 2.04 (s, 3H, ^{2}J(PtH) = 70 Hz, PtMe), 7.5 (m, 2H, H^{5}, H$^{5'}$), 7.80 (dd, 1H, ^{3}J(H^{3}H^{4}) = 8 Hz, ^{4}J(H^{3}H^{5}) = 1 Hz, H^{3}), 7.92 (dd, 1H, ^{3}J(H$^{3'}$H$^{4'}$) = 8 Hz, ^{4}J(H$^{3'}$H$^{5'}$) = 2 Hz, H$^{3'}$), 8.04 (ddd, 1H, ^{3}J(H^{4}H^{3}) = 8 Hz, ^{3}J(H^{4}H^{5}) = 8 Hz, ^{4}J(H^{4}H^{6}) = 1 Hz, H^{4}), 8.11 (ddd, 1H, ^{3}J(H$^{4'}$H$^{3'}$) = 8 Hz, ^{3}J(H$^{4'}$H$^{5'}$) = 9 Hz, ^{4}J(H$^{4'}$H$^{6'}$) = 1 Hz, H$^{4'}$), 8.50 (dd, 1H, ^{3}J(H$^{6'}$H$^{5'}$) = 6 Hz, ^{4}J(H$^{6'}$H$^{4'}$) = 1 Hz, H$^{6'}$), 9.21 (dd, 1H, ^{3}J(H^{6}H^{5}) = 6 Hz, ^{4}J(H^{6}H^{4}) = 1 Hz, H^{6}). ESI-MS: *m*/*z* 614.1; calcd for [Pt(C$_8$H$_5$O$_4$)Me$_2$(dpkOH)-Na]$^{+}$ 614.1. IR (Nujol mull, cm^{-1}): 1652 ν(CO), 1605 ν(CO). Anal. Calcd for $C_{21}H_{20}N_2O_6Pt$: C, 42.63; H, 3.41; N, 4.74. Found: C, 42.94;

H, 3.66; N, 4.62. *trans*-[$PtMe_2(O_2CC_6H_4CO_2H)$(dpkOH)], **7**: NMR in methanol-d_4: $\delta(^1H)$ 1.64 (s, 6H, $^2J(PtH)$ = 70 Hz, PtMe), 7.50 (dd, 2H, $^2J(H^5H^4)$ = 8 Hz, $^2J(H^5H^4)$ = 5 Hz, H^5), 7.52−7.92 (m, 4H, phth), 7.80 (d, 2H, $^3J(H^3H^4)$ = 8 Hz, $^4J(H^3H^5)$ = 1 Hz, H^3), 8.07 (dd, 2H, $^3J(H^4H^3)$ = 8 Hz, $^3J(H^4H^5)$ = 8 Hz, H^4), 9.05 (d, 2H, $^3J(H^6H^5)$ = 5 Hz, $^4J(H^6H^4)$ = 1 Hz, H^6).

X-ray Structure Determinations. The crystals were mounted on a glass fiber, and data were collected at 150(2) K by using a Bruker Smart Apex II CCD diffractometer. The unit cell parameters were calculated and refined from the full data set, and the structure was solved and refined by using the SHELX software.[23] Details are given in Table S1 and in the CIF files. The hydrogen atoms of the water molecules in complex **4**·$4.5H_2O$ could not be located, so the water molecules were treated as O-atoms only.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1 and Table S1. Crystallographic data in electronic CIF form only is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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