Carbon−Oxygen Bond Formation at Metal(IV) Centers: Reactivity of Palladium(II) and Platinum(II) Complexes of the [2,6-(Dimethylaminomethyl)phenyl-*N*,*C*,*N*]$^-$ (Pincer) Ligand toward Iodomethane and Dibenzoyl Peroxide; Structural Studies of M(II) and M(IV) Complexes

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The presence of the [2,6-(dimethylaminomethyl)phenyl-*N*,*C*,*N*]$^-$ (pincer) ligand (NCN) in platinum(II) complexes has been used to generate stable organoplatinum(IV) complexes that model possible intermediates and reactivity in metal-catalyzed C−O bond formation processes. The complexes M(O_2CPh)(NCN) [M = Pd (**1**), Pt (**2**)] were obtained by metathesis reactions from the chloro analogues, and although **1** does not react with dibenzoyl peroxide, **2** does so to form Pt(O_2CPh)$_3$(NCN) (**3**) as a model intermediate for the acetoxylation of arenes by acetic acid in the presence of palladium(II) acetate and an oxidizing agent. The complex Pt(O_2CPh)(NCN) (**2**) reacts with iodomethane in a complex manner to form PtI(NCN) (**6**) and *cis*-Pt(O_2CPh)$_2$Me(NCN) (**7**). Complex **7** decomposes to form Pt(O_2CPh)(NCN) (**2**) and MeO_2CPh, probably via benzoate dissociation followed by nucleophilic attack by the benzoate ion at the Pt^{IV}-Me carbon atom. The Pd(II) analogue Pd(O_2CPh)(NCN) (**1**) reacts with MeI to give PdI(NCN) (**8**) and MeO_2CPh, for which the potential intermediacy of Pd(IV) species could not confirmed by ^{1}H NMR spectroscopy. The complex PtTol(NCN) (**4**) (Tol = 4-tolyl) reacts with $(PhCO_2)_2$ to form *cis*-Pt(O_2CPh)$_2$Tol(NCN) (**5**), but, unlike the Pt^{IV}Me analogue **7**, the Pt^{IV}Tol complex **5** does not undergo facile C−O bond formation. X-ray structural studies of the isostructural square-planar complexes M(O_2CPh)(NCN) (**1**, **2**) and of the octahedral Pt(IV) complexes as solvates **3**·1/2Me_2CO, **5**·Me_2CO, and **7**·Me_2CO·H_2O are reported. Complexes **5** and **7** have *cis*-PtC_2 and *cis*-Pt(O_2CPh)$_2$ configurations.

Introduction

The formation of arene−oxygen bonds is an important process in organic synthesis, and considerable advances have been reported in catalysis involving coupling of carbon and oxygen atoms using palladium catalysts for which mechanistic evidence for the involvement of Pd^{II}-C and Pd^{II}-O centers is established.[1,2] In addition, there are reports of C−O coupling employing other palladium species under quite different reaction conditions where evidence for Pd(IV) involvement has been presented.[3−12] However, in these studies Pd(IV) intermediates containing both Pd−C and Pd−O bonds that

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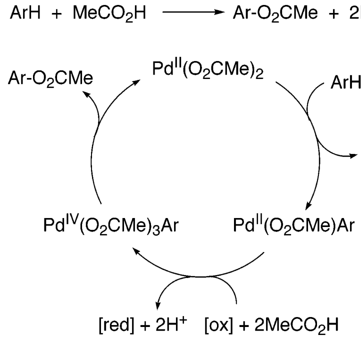

Figure 1. Acetoxylation of arenes in acetic acid catalyzed by palladium(II) in the presence of an oxidant. The number of ligands coordinated to Pd(II) and Pd(IV) is arbitrarily set at two and four, respectively; Pd(II) and Pd(IV) species are assumed to have square-planar and octahedral coordination, respectively, where the number of carboxylate ligands depends on their coordination mode in achieving these geometries.

lead directly to C−O coupling have not been observed spectroscopically. In contrast to systems where Pd^{II}−C and Pd^{II}−O bonds are present in key intermediates, reactions in which Pd(IV) intermediacy is proposed have involved the presence of strong oxidizing agents. These have included chromium(VI);[4] molybdenum(VI);[5] peracids;[6] *tert*-butylhydroperoxide;[6g,h;8,9] Bu^{t}OOH in combination with vanadium(V),[7b,c] rhodium(I),[7c] or an iron(III) porphyrin complex;[6g,h;8] IOPh;[9] IO(C_6F_5);[6g,h] IPh(O_2CMe)$_2$;[10,12] dibenzoylperoxide;[11] or an iron(III) porphyrin complex in combination with peracids,[6g,h] IO(C_6F_5),[6h] or hydrogen peroxide.[13] Most of the reactions studied involve addition of the oxidizing agent to preformed organopalladium(II) complexes.[5−9,11,13] The catalytic process illustrated by Figure 1 is assumed to occur via palladation of the arene (for which there are ample precedents)[14] followed by oxidation of Pd(II) to Pd(IV) and subsequent C−O reductive elimination from a Pd(IV) species,[4a,c,10,12] e.g., [Pd^{IV}(O_2CMe)$_n$Ar]$^{3-n}$.

In a model system related to this reactivity, the reaction of PdMeR(bpy) (R = Me,[11a−c,e] Tol;[11d,e] bpy = 2,2′-bipyridine) with dibenzoyl peroxide, Pd(IV) intermediates containing both Pd^{IV}−R and Pd^{IV}−O_2CPh bonds were observed by NMR spectra. However, these species are intermediates in the formation of Pd(O_2CPh)R(bpy) (R = Me, Ar), and the R−O bonds are formed in subsequent reactions of Pd(O_2CPh)R(bpy) with (PhCO$_2$)$_2$.[11c−e] These reports illustrate the need for caution in deducing that Pd(IV) intermediates occur in key product formation steps on the basis of detection of Pd(IV) species.[3,11c−e] In view of the detection of Pd(IV) species in this system, the important role of intramolecular coordination in other systems studied to date ([CN],[5b,6b,7,9,12] [CNO],[6b] [CNS],[6c−h,9,13] [CNN][5]), and an enhanced possibility for stabilization of Pd(IV) intermediates by intramolecular coordination,[15] we commenced a study of the reactivity of dibenzoyl peroxide toward Pd^{II}(NCN) intramolecular complexes containing the archetypal pincer group [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$ (Figure 2). This work was subsequently extended to Pt(II) systems as a model for reactivity similar to that expected for Pd(II), noting the reported reaction of PtPh$_2$(bpy) with (PhCO$_2$)$_2$ to form Pt(O_2CPh)$_2$Ph$_2$(bpy)[16] as a guide to reactivity, together with considerable current interest in C−O bond formation at Pt(IV) centers.[17,18] The synthesis and decomposition of complexes containing the M^{II}(NCN) and Pt^{IV}(NCN) moieties are described herein.

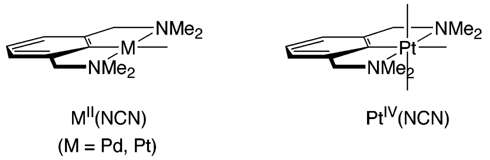

Figure 2. Pincer ligand systems coordinated to M(II) and Pt(IV) centers.

Results

Reactivity Studies. The complexes M(O_2CPh)(NCN) [M = Pd (**1**), Pt (**2**)] were chosen for initial studies so that the anticipated reactions with (PhCO$_2$)$_2$ would provide for a simple carboxylate donor set similar to that envisaged for the catalytic system of Figure 1. They were obtained in yields of 98% (Pd) and 95% (Pt) from the reaction of the chloro complexes with silver(I) benzoate, and structural studies of **1** and **2** are described below.

The palladium complex **1** did not react with (PhCO$_2$)$_2$ when studied by ^{1}H NMR spectroscopy at ambient temperature over several days. However, reaction of the platinum complex **2** gave spectra consistent with the formation of Pt(O_2CPh)$_3$(NCN) (**3**). This complex was subsequently isolated in a preparative study in 68% yield (eq 1) and crystallized for a structural analysis (see below).

$$\begin{array}{l}\mathrm{M^{II}(O_2CPh)(NCN)} \\ \mathbf{1}\text{: } \mathrm{M = Pd\ (no\ reaction)} \\ \quad \mathbf{2}\text{: } \mathrm{M = Pt}\end{array} + \mathrm{(PhCO_2)_2} \xrightarrow{25\ ^\circ\mathrm{C}} \underset{\mathbf{3}}{\mathrm{Pt^{IV}(O_2CPh)_3(NCN)}} \quad (1)$$

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Although the Pt(IV) complex **3** is a suitable model for oxidation of **1**, its reluctance to decompose by C−O coupling involving the intramolecularly stabilized $\mathrm{Pt^{IV}{-}C}$ bond led us to examine the reactivity of PtTol(NCN) (**4**) (Tol = 4-tolyl), which contains a simple $\mathrm{Pt^{II}{-}Ar}$ group supported by the pincer ligand. The 4-tolyl group was chosen to facilitate NMR studies of reactivity, to give the presence of an aryl group different from that in the oxidizing agent, and in view of the X-ray structural characterization reported for the related complex *cis*-$\mathrm{PtI_2Tol(NCN)}$.[19] Complex **4** can be regarded as a *trans*-diorganoplatinum(II) analogue of reagents known to be oxidized by dibenzoyl peroxide, *cis*-$\mathrm{PtPh_2(bpy)}$,[16] and *cis*-PdMe(Tol)(bpy);[11d] Pd(II) analogues of **4** are unstable.[20] When studied by ^{1}H NMR spectroscopy in acetone-d_6 at 25 °C, complex **4** was found to react with $(\mathrm{PhCO_2})_2$ to give resonances consistent with the presence of *cis*-$\mathrm{Pt(O_2CPh)_2Tol(NCN)}$ (**5**) (eq 2) together with decomposition products including $\mathrm{Pt(O_2CPh)(NCN)}$ (**2**) (see below).

$$\underset{\mathbf{4}}{\mathrm{Pt^{II}Tol(NCN)}} + (\mathrm{PhCO_2})_2 \xrightarrow{25\ °\mathrm{C}} \underset{\mathbf{5}}{cis\text{-}\mathrm{Pt^{IV}(O_2CPh)_2Tol(NCN)}} \quad (2)$$

Isolation of complex **5** from this reaction was unsuccessful, but **5** could be synthesized independently by addition of silver(I) benzoate to *cis*-$\mathrm{PtI_2Tol(NCN)}$, giving crystals suitable for a structural analysis (see below).

Complex **5** was found to be stable to >90 °C when examined by ^{1}H NMR spectroscopy in toluene-d_8, and this led us to explore a similar system containing a Pt−C(sp^3) bond rather than the Pt−C(sp^2) bonds in **4** and **5** in a search for a system that would undergo C−O bond formation. However, Pt(II) reagents analogous to **4** but containing Pt-alkyl groups are not known, so an alternative strategy was explored to attempt the synthesis of a $\mathrm{Pt^{IV}Me}$ analogue of **5**. In a reaction at 0 °C in acetone-d_6 studied by ^{1}H NMR spectroscopy, $\mathrm{Pt(O_2CPh)(NCN)}$ (**2**) was found to react with MeI to give resonances consistent with the formation of PtI(NCN) (**6**) and *cis*-$\mathrm{Pt(O_2CPh)_2Me(NCN)}$ (**7**); under the same conditions complex **7** decomposed by C−O coupling to form $\mathrm{MeO_2CPh}$ and complex **2**. The overall reaction is interpreted as in eq 3 and 4.

$$2\ \underset{\mathbf{2}}{\mathrm{Pt^{II}(O_2CPh)(NCN)}} + \mathrm{MeI} \xrightarrow{0\ °\mathrm{C}} \underset{\mathbf{6}}{\mathrm{Pt^{II}I(NCN)}} + \underset{\mathbf{7}}{cis\text{-}\mathrm{Pt^{IV}(O_2CPh)_2Me(NCN)}} \quad (3)$$

$$\underset{\mathbf{7}}{cis\text{-}\mathrm{Pt^{IV}(O_2CPh)_2Me(NCN)}} \xrightarrow{0\ °\mathrm{C}} \underset{\mathbf{2}}{\mathrm{Pt^{II}(O_2CPh)(NCN)}} + \mathrm{MeO_2CPh} \quad (4)$$

A synthetic method for **7** was sought to allow its isolation in the absence of both its decomposition product **2** and the iodo complex **6**. It was found that PtI(NCN) (**6**) reacts readily with silver(I) benzoate to form $\mathrm{Pt(O_2CPh)(NCN)}$ (**2**) (eq 5), and thus when excess MeI and excess silver(I) benzoate were added to **2**, complex **7** was able to be separated from silver iodide in 71% yield and crystals were obtained for a structural analysis (see below). The process is assumed to be accompanied by some decomposition of **7** to give **2**, which reacts with MeI to give **7**, thus ensuring that eventually the only complex in solution is the desired product (**7**). Silver(I) benzoate reacts with MeI at a comparable rate to the overall reaction to form $\mathrm{MeO_2CPh}$, so that this reaction may also be assumed to be occurring during the synthesis of **7**.

$$\underset{\mathbf{6}}{\mathrm{Pt^{II}I(NCN)}} + \mathrm{Ag[O_2CPh]} \rightarrow \underset{\mathbf{2}}{\mathrm{Pt^{II}(O_2CPh)(NCN)}} + \mathrm{AgI} \quad (5)$$

The decomposition of the pure complex **7** was confirmed as shown in eq 4, and NMR studies of the reaction at 50 °C revealed first-order behavior with rate constants of $2.47 \times 10^{-4}\ \mathrm{s^{-1}}$ in acetone-d_6 and $1.04 \times 10^{-4}\ \mathrm{s^{-1}}$ in toluene-d_8.

The Pd(II) complex $\mathrm{Pd(O_2CPh)(NCN)}$ (**1**) was found to react with MeI at a higher temperature (~25 °C) than the Pt(II) analogue (~0 °C), to give PdI(NCN) (**8**) and $\mathrm{MeO_2CPh}$ (eq 7), but a Pd(IV) intermediate (if formed) could not be detected by ^{1}H NMR spectroscopy.

$$\underset{\mathbf{1}}{\mathrm{Pd^{II}(O_2CPh)(NCN)}} + \mathrm{MeI} \xrightarrow{25\ °\mathrm{C}} \underset{\mathbf{8}}{\mathrm{Pd^{II}I(NCN)}} + \mathrm{MeO_2CPh} \quad (6)$$

Spectroscopic Characterization of New Complexes. Complexes **1**−**3**, **5**, and **7** give ^{1}H NMR spectra showing integration as expected for formulas presented. The complexes $\mathrm{M(O_2CPh)(NCN)}$ (**1**, **2**) and $\mathrm{Pt(O_2CPh)_3(NCN)}$ (**3**) show a singlet for the methylene protons and satellites for $^3J_{\mathrm{Pt-H}}$ 38 Hz for **2** and 28 Hz for **3**. For the Pt(IV) complexes **5** and **7** these protons are differentiated into two doublets with $^3J_{\mathrm{Pt-H}}$ 31−39 Hz for **5** and **7** (obscured for **3**). In a similar manner the M(II) complexes exhibit a singlet for $\mathrm{NMe_2}$ ($^3J_{\mathrm{Pt-H}}$ 38 Hz for **2**), but two singlets for the Pt(IV) complexes ($^3J_{\mathrm{Pt-H}}$ 25−39 Hz for **5** and **7**). Spectra for complex **5** show characteristic features discussed in detail for *cis*-$\mathrm{PtI_2(Tol)(NCN)}$;[19] for example, the 4-tolyl group in **5** shows $^3J_{\mathrm{Pt-H}}$ 29 and 40 Hz for the differentiated 2,6-protons of the 4-tolyl group. The methyl group in *cis*-$\mathrm{Pt(O_2CPh)_2Me(NCN)}$ (**7**) has $^3J_{\mathrm{Pt-H}}$ 70 Hz, and spectra for **3**, **5**, and **7** showed two benzoate environments.

Structural Studies of 1 and 2 and Solvates of 3, 5, and 7. The results of the low-temperature single-crystal X-ray structure determinations are consistent with the stoichiometries, connectivities, and stereochemistries mentioned above (Figures 3 and 4). Molecules of **1**, **2**, **5**, and **7** are devoid of crystallographic symmetry, but **3**, as modeled in space group *C*2/*c*, lies disposed on a crystallographic 2-fold axis. Crystals containing **3**, **5**, and **7** were modeled as acetone (and water) solvates. Although the refinements of $\mathbf{3}\cdot 1/2\mathrm{Me_2CO}$ and $\mathbf{7}\cdot\mathrm{Me_2CO}\cdot\mathrm{H_2O}$ are diminished in their useful-

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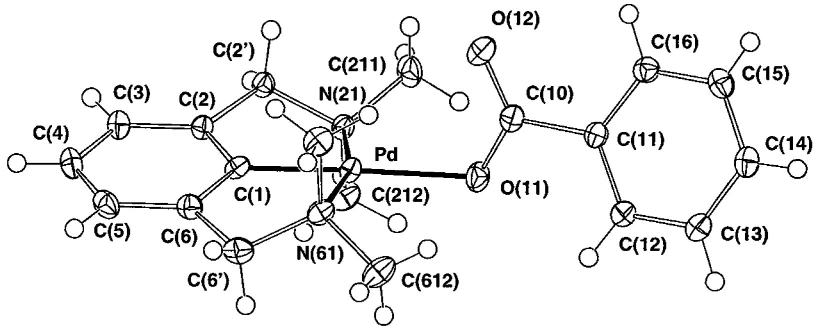

Figure 3. Projection of a molecule of $Pd(O_2CPh)(NCN)$ (**1**), which is isomorphous with the platinum(II) analogue **2**.

ness because of the disorder/refinement anomalies, the precision overall enables some useful comparisons (Table 1).

In all five complexes the pincer group is present as a *mer*-terdentate, the chelate arms of the same chirality, so that the M(NCN) array has a quasi-, or in the case of the model for **3**, exact 2-symmetry, the M−C bond lying on the (putative) 2-axis. The chelate rings have quasi-envelope conformations, the nitrogen atoms being at the flaps, so that one of the methyl substituents is "equatorial" and quasi-coplanar with the M(NCN) array, and the other "axial", such that the two axial methyls are disposed to either side of the M(NCN) plane. Differences in the torsion angles of the two chelates in all cases are no more than a few degrees, despite any (inherent) asymmetry of the substituent array in the other coordination site(s). The consistent chirality within each ligand is associated with a twist in the disposition of the central C_6 plane with respect to the CN_2O coordination plane. In all (unidentate) benzoate systems, the carboxylate is quasi-coplanar with its aromatic ring.

The metal(II) complexes **1** and **2** are isomorphous and have approximate square-planar coordination (Figure 1), where the maximum deviation from the "CN_2O" mean planes is 0.009(1) Å for **1** (Table 1). In the metal(II) complexes, the M−C and M−O distances do not differ nontrivially, but the Pd−N distances are ~0.02 Å longer than their Pt−N counterparts. These trends are consistent with other reports of isostructural organometal pairs in which Pd−N, P, O, S, and Cl distances are similar to or longer than the Pt analogues.[21−25]

In the triad of Pt(IV) complexes, despite the increase in oxidation state, metal−ligand distances are increased compared with the M(II) complexes, in keeping with the increase in coordination number. The additional carbon atoms bound to the metal in **5** and **7** lie cis to the tridentate, as found for *cis*-PtI_2(Tol-4)(NCN).[19] The planes of the additional pair of trans "axial" ligands lie quasi-parallel to the CO_3 (**3**) and C_2O_2 (**5**, **7**) vertical coordination planes, their uncoordinated carboxylate oxygen atoms lying above (and below) the central C(1) donor of the tridentate. In **5**, the 4-tolyl plane makes a dihedral angle of 10.8(1)° with the "vertical" C(1,01)O(11,21) coordination plane.

Excluding consideration of **3**, affected by disorder, the Pt−O distances are similar, regardless of their location in the coordination sphere, although there is a significant difference between the "axial" values in **5** and **7**, perhaps in consequence of differing trans-influences of methyl compared with 4-tolyl. The very short distance [2.004(4) Å] found in **3** for the "axial" Pt−O(21) distance, which may be only slightly affected by disorder, may reflect the greater difference in trans-influence induced by replacement of the carbon donor by oxygen. The associated O−Pt−C,O trans-angles in all these complexes are well removed from 180°, bowing away from the tridentate, presumably in response to the diminished angle imposed by the N−Pt−N group. An interesting feature of the array of structures is the manner in which the M−O−C (carboxylate) angles vary; these are similar for **1** and **2**, both lying well below their counterparts for **3**, **5**, and **7**, where, in turn, the "axial" sites have larger angles. The diminution in M−O(11)−C(11) in the M(II) complexes, compared with Pt−O(n1)−C(n1) of the Pt(IV) complexes, may be a consequence of the less crowded coordination sphere, permitting a less strained environment and a closer approach of O(n2) to the metal center, even if actual coordination does not occur.

We also note a considerable asymmetry in the exocyclic Pt−C(01)−C(02,6) angles at the 4-tolyl donor in **5** [126.5(3)°, 117.0(3)°]; H(06)···O(11) is short [2.1_7 Å (est.)] as also are H(02)···C(1), H(6′a) [2.6_0, 2.2_7 (est.)]. A similar asymmetry occurs in the Pd(IV) cation $[Pd(CH_2Bu^t)Ph(C{\sim}N)(bpy)]^+$ (C~N = 8-methylquinolinyl), which has Pd−C(01)−C(02,06) angles of 127.6(3)° and 113.7(4)°.[15b]

Discussion

The reaction of eq 3, involving oxidation of Pt(II) by iodomethane, is not directly related to possible steps in the catalysis of Figure 1 but does involve interesting processes in which the methyl group and iodine atom become bonded to different platinum centers and where there is transfer of a benzoate group between platinum centers. It has been established that a wide range of organoplatinum(II) complexes undergo oxidative addition with iodomethane via the S_N2 mechanism, and for some systems NMR spectra indicate the presence of

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cationic Pt(IV) intermediates such as *fac*-[$Pt^{IV}Me_3$(bpy)-(solvent)]$^+$ and thus iodide ion formation prior to coordination to form *fac*-$Pt^{IV}IMe_3$(bpy).[26] We have found that the reagent in eq 3, Pt(O_2CPh)(NCN) (**2**), reacts with sodium iodide to form PtI(NCN) (**6**), and thus a likely mechanism for the reaction of eq 3 is as shown in eqs 7–9, in which formation of the cation [Pt^{IV}(O_2CPh)-Me(NCN)]$^+$ (eq 7) is followed by anion exchange (eq 8) and coordination of benzoate to the cation to give **7** (eq 9). There are precedents for five-coordinate organoplatinum(IV)[27a] and Pd(IV)[27b] species, although solvent or bidentate benzoate coordination in the cation to give six-coordination cannot be discounted. Bidentate coordination would be consistent with views that occurrence of additional coordination at d^8 centers may facilitate oxidative addition,[28] in particular for systems with an uncoordinated group in the reagent, e.g., during the oxidative addition of iodomethane to RhCl{B(pz)$_3$-*N,N'*}(L) (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, CO).[28c]

$$\underset{\mathbf{2}}{Pt^{II}(O_2CPh)(NCN)} + MeI \rightarrow [Pt^{IV}(O_2CPh)Me(NCN)]^+ + I^- \quad (7)$$

$$\underset{\mathbf{2}}{Pt^{II}(O_2CPh)(NCN)} + I^- \rightarrow \underset{\mathbf{6}}{Pt^{II}I(NCN)} + PhCO_2^- \quad (8)$$

$$\underset{\mathbf{2}}{[Pt^{IV}(O_2CPh)Me(NCN)]^+} + PhCO_2^- \rightarrow \underset{\mathbf{7}}{cis\text{-}Pt^{IV}(O_2CPh)_2Me(NCN)} \quad (9)$$

Equations 1 (M = Pt) and 2 represent models for the oxidation step in the catalytic process of Figure 1 to give "$M^{IV}(O_2CR)_nAr$", although noting the qualification that the palladium analogues are unreactive (eq 1) or not readily accessible for study (eq 2) under the current conditions. The reaction of eq 2 can be regarded as oxidative addition of $(PhCO_2)_2$ to a *trans*-$Pt^{II}C_2N_2$ moiety, in contrast to the oxidative addition to a *cis*-$Pt^{II}C_2N_2$ moiety in $PtPh_2$(bpy).[16]

Reductive elimination via C–O bond formation in the catalysis of Scheme 1 is modeled by eq 4, with Pt(IV) rather than Pd(IV) in the model reaction, except that C–O bond formation is occurring from a C(sp^3) center in eq 4. Reductive elimination by C–O bond formation from *cis*-$Pt^{IV}(O_2CPh)_2$Me(NCN) (**7**) (eq 4) can be most readily accounted for by the occurrence of the mechanism proposed for decomposition of *fac*-$Pt^{IV}(O_2CMe)Me_3$-(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane]. For the diphosphine complex, kinetic data support a mechanism in which acetate dissociation is followed by nucleophilic attack at the methyl group to give MeO_2-CMe.[18] Thus, it is feasible that complex **7** may decompose via benzoate dissociation and formation of a five-coordinate cationic species [$Pt^{IV}(O_2CPh)$Me(NCN)]$^+$,

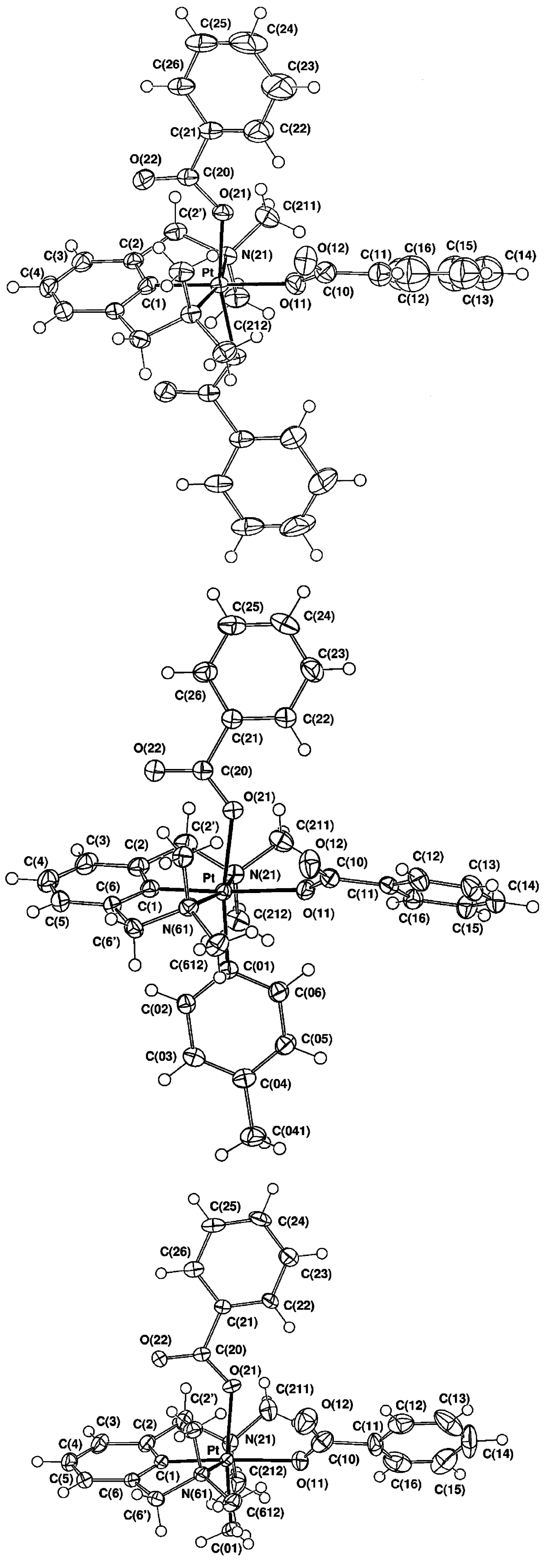

Figure 4. Projections of molecules of (a) $Pt(O_2CPh)_3$(NCN) (**3**) in the solvate complex **3**·1/2Me_2CO [a crystallographic 2-fold axis through Pt–C(1)]: only one of the pair of disordered components of benzoate 1 is shown. (b) Pt(O_2-$CPh)_2$Tol(NCN) (**5**) in **5**·Me_2CO. (c) $Pt(O_2CPh)_2$Me(NCN) (**7**) in **7**·Me_2CO·H_2O.

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Table 1. Selected Bond Distances (Å) and Angles (deg) and Other Data for $M(O_2CPh)(NCN)$ [M = Pd (1), Pt (2)] and 3, 5, and 7 in Their Solvates $Pt(O_2CPh)_3(NCN)\cdot 1/2Me_2CO$, $Pt(O_2CPh)_2Tol(NCN)\cdot Me_2CO$, and $Pt(O_2CPh)_2Me(NCN)\cdot Me_2CO\cdot H_2O$, where NCN = [2,6-(Dimethylaminomethyl)phenyl-*N*,*C*,*N*]$^-$

	1	**2**	**3**·1/2Me_2CO	**5**·Me_2CO	**7**·$Me_2CO\cdot H_2O$
			Bond Distances		
M−C(1)	1.895(2)	1.906(2)	1.951(5)	1.949(4)	1.935(5)
M−N(21, 61)	2.099(2), 2.103(2)	2.080(2), 2.080(2)	2.116(3)	2.135(3), 2.134(3)	2.137(6), 2.120(5)
M−O(11, 21)	2.140(1)	2.143(2)	2.145(6), 2.004(4)	2.144(3), 2.121(3)	2.144(5), 2.169(4)
Pt−C(01)				2.036(4)	2.045(6)
C(10)−O(11, 12)	1.279(2), 1.240(2)	1.275(3), 1.238(3)	1.31(1), 1.24(1)	1.288(5), 1.232(4)	1.225(9), 1.245(9)
C(20)−O(21, 22)			1.320(5), 1.192(5)	1.280(5), 1.235(4)	1.273(6), 1.236(7)
			Bond Angles		
C(1)−M−N(21, 61)	81.68(7), 81.33(7)	82.15(10), 82.22(10)	82.13(9) (x2)	82.1(1), 81.1(1)	81.9(2), 81.0(2)
N(21)−M−N(61)	163.01(6)	164.37(9)	164.3(1)	163.2(1)	162.8(2)
O(11)−M−C(1)	177.43(7)	177.64(10)	173.3(2)	173.9(1)	173.1(2)
O(11)−M−N(21, 61)	100.67(6), 96.32(6)	100.11(8), 95.51(9)	104.0(3), 91.8(3)	92.4(1), 104.4(1)	92.5(2), 104.7(2)
O(21)−Pt−N(21, 61)			87.3(1), 94.8(1)	85.5(1), 95.6(1)	84.1(2), 95.5(2)
O(21)−Pt−O(11)			80.4(4), 84.9(4)	80.5(1)	86.2(2)
O(21)−Pt−C(1, 01)			97.38(8), 165.2(1)	96.4(1), 169.9(1)	97.2(2), 172.2(2)
C(01)−Pt−N(21, 61)			94.8(1), 87.3(2)	91.9(1), 89.8(1)	93.6(2), 88.8(2)
C(01)−Pt−C(1)			97.38(8)	92.9(2)	89.9(2)
M−C(1)−C(2,6)	119.2(1), 119.6(1)	119.0(2), 118.8(2)	117.6(2) (x2)	117.4(2), 119.0(3)	117.5(4), 118.8(4)
M−O(11)−C(10)	117.0(1)	119.2(1)	128.1(6)	129.2(2)	125.7(5)
Pt−O(21)−C(20)			133.3(3)	135.2(3)	132.6(4)
Pt−C(01)−C(02, 06)				126.5(3), 117.0(3)	

followed by nucleophilic attack by the benzoate group at the methyl group, which is activated by cation formation, eliminating MeO_2CPh and $Pt^{II}(O_2CPh)(NCN)$. Consistent with an ionic or polar mechanism the reaction proceeds at a rate in acetone about twice that in toluene.

The reaction of eq 6 involves C−O bond formation, but the intermediacy of Pd(IV), via reactions analogous to eq 3 followed by eq 4 or via other Pd(IV) species, has not been confirmed by NMR spectroscopy.

The high stability of the 4-tolyl complex, *cis*-$Pt^{IV}(O_2CPh)_2Tol(NCN)$ (**5**), compared with the methyl analogue (**7**) may be related to steric congestion at the *ipso*-carbon of the Tol group resulting from the close proximity of two NMe_2 groups of the pincer ligand. Space-filling models indicate that interaction of a benzoate oxygen with the *ipso*-carbon, normal to the 4-tolyl plane, is prevented for both intramolecular coupling and external attack by a benzoate ion.

Oxidative addition of dibenzoyl peroxide is demonstrated to occur at a d^8 monoarylmetal(II) species (eq 1), and formation of C−O bonds on reaction of iodomethane with a benzoatopalladium(II) species (eq 6). The high stability of *cis*-$Pt^{IV}(O_2CPh)_2Tol(NCN)$ (**5**) compared with *cis*-$Pt^{IV}(O_2CPh)_2Me(NCN)$ (**7**) suggests that $C(sp^2)$−O bond formation may be elusive for Pt(IV) complexes where the *ipso*-carbon is sterically protected. Thus, a model reaction for the step in palladium catalysis (Figure 1) involving $C(sp^2)$−O bond formation at Pt(IV) centers may not be readily accessible for the intramolecular system chosen for the present study. However, organopalladium(IV) species undergo intramolecular $C(sp^2)$−$C(sp^3)$ reductive elimination processes much more readily than Pt(IV); for example, *fac*-$Pd^{IV}IMe_2Ph(bpy)$ reductively eliminates ethane and toluene at 0 °C,[29] but *fac*-$Pt^{IV}IMe_2Ph(bpy)$ is stable at ambient temperature.[30] Ligand dissociation is expected to be a preliminary step in the intramolecular reductive elimination process for Pd(IV),[3,31] and also for elimination from *cis*-$Pt^{IV}(O_2CPh)_2Me(NCN)$ as discussed above, and thus is expected to be facile for reactions of Scheme 1 where the ancillary ligands in potential Pd(IV) intermediate(s) are limited to monodentate and/or bidentate acetate ions. It is feasible that one-electron oxidation of arylpalladium(II) species may facilitate C−O coupling in the catalysis of Figure 1, but this would seem unlikely for the reaction of eq 6, where the oxidant is iodomethane; it would be in contrast with demonstrated two-electron Pt(II)/Pt(IV) reactivity (eqs 1, 2, 4) and the NMR detection of Pd(IV) species $Pd(O_2CPh)Me_2R(bpy)$ in the complex reaction of PdMeR(bpy) (R = Me,[11c,e] Tol[11d,e]) with $(PhCO_2)_2$ and the lack of evidence for Pd(III) as an oxidation state in organometallic chemistry.[32]

The reactions described herein exhibit novel mechanistic aspects, and although they are principally concerned with platinum rather than palladium, they do provide some guidance for understanding the catalysis reaction of Figure 1, where the coordination environment of palladium is dominated by acetate ligands, e.g., acetoxylation of benzene [$MeCO_2H/Pd(O_2CMe)_2/IPh(O_2CMe)_2$][10] and, in particular, benzo[*h*]quinoline [$MeCN/Pd(O_2CMe)_2/IPh(O_2CMe)_2$] at $C(10)(sp^2)$ and 8-methylquinoline [$MeCO_2H/Pd(O_2CMe)_2/IPh(O_2CMe)_2$] at $C(sp^3)$ reported[12] after completion of the work described herein. The latter reactions are expected to proceed via Pd(IV) intermediates involving cyclopalladated species.[12]

Experimental Section

All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an argon atmosphere using Schlenk techniques. Solvents were purified and dried in the normal manner.[33] Other reagents were purchased and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer operating at 199.975 MHz (^1H) or a Varian Unity Inova 400

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WB spectrometer operating at 100.587 (^{13}C) and 399.703 (^{1}H) MHz. Chemical shifts are reported in ppm relative to $SiMe_4$. Microanalyses were performed by the Central Science Laboratory, University of Tasmania. Mass spectra were recorded on a Kratos Concept ISQ mass spectrometer using the LSIMS technique in a 3-nitrobenzoyl matrix and an *m/z* scanning range of 50−1500 with an 8 kV probe.

The reagents $MX(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (X = Cl, I; M = Pd, Pd),[34] *cis*-$PtI_2Tol(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$,[19] and $Ag[O_2CPh]$ [35] were prepared as described; $PtTol(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (**4**) was obtained by a method modified from that reported,[20] and dibenzoyl peroxide was used as received (BDH).

Synthesis of $Pd(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (1). A solution of $PdCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (0.12 g, 0.36 mmol) in acetone (5 mL) was added to silver benzoate (0.09 g, 0.39 mmol). The suspension was stirred for 1 h in the absence of light and then filtered through Celite. The filtrate was concentrated in a vacuum and pentane added to precipitate the product. The resulting white solid was isolated, washed with pentane (3 × 2 mL), and dried in a vacuum. Yield: 0.15 g (98%). ^{1}H NMR (acetone-d_6): δ 8.06 (m, 2H, H2,6-Ph), 7.4−7.3 (m, 3H, H3,4,5-Ph), 6.94 (dd, 1H, ^{3}J = 7.8 Hz and ^{3}J = 6.6 Hz, H4-NCN), 6.79 (d, 2H, ^{3}J = 7.5 Hz, H3,5-NCN), 4.05 (s, 4H, NCH_2), 2.89 (s, 12H, NMe). ^{13}C NMR (acetone-d_6): δ 171.70 (C═O), 146.47 (NCN), 130.33 (Ph), 128.15 (Ph), 124.94 (NCN), 120.35 (NCN), 74.70 (NCH_2), 52.18 (NMe). LSIMS (in mnba): *m/z* 418.1 ($[M]^+$, 3.5%), 297.1 ($[M - PhCO_2]^+$, 100%). Anal. Calcd: C, 54.49; H, 5.78; N, 6.69. Found: C, 54.72; H, 5.65; N, 6.82.

Synthesis of $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (2). A solution of $PtCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (0.16, 0.38 mmol) in acetone (5 mL) was added to silver benzoate (0.09 g, 0.39 mmol). The suspension was stirred overnight in the absence of light and then filtered through Celite. The filtrate was concentrated in a vacuum and pentane added to precipitate the product. The resulting white solid was isolated, washed with pentane (3 × 2 mL), and dried in a vacuum. Yield: 0.18 g (95%). ^{1}H NMR (acetone-d_6): δ 8.10 (m, 2H, H2,6-Ph), 7.4−7.3 (m, 3H, H3,4,5-Ph), 6.92 (dd, 1H, ^{3}J = 8.5 Hz and ^{3}J = 6.3 Hz, H4-NCN), 6.79 (d, 2H, ^{3}J = 7.7 Hz, H3,5-NCN), 4.08 (s, 4H, $^{3}J_{Pt-H}$ = 49 Hz, NCH_2), 3.05 (s, 12H, $^{3}J_{Pt-H}$ = 38 Hz, NMe). ^{13}C NMR (acetone-d_6): δ 172.34 (C═O), 145.61 (NCN), 140.47 and 139.43 (NCN and Ph), 130.87 (Ph), 130.39 (Ph), 128.39 (Ph), 124.43 (NCN), 119.96 (NCN), 77.29 (NCH_2), 53.80 (NMe). LSIMS (in mnba): *m/z* 507.1 ($[M]^+$, 7%), 385.1 ($[M - PhCO_2H]^+$, 100%). Anal. Calcd: C, 44.96; H, 4.77; N, 5.52. Found: C, 44.86; H, 4.60; N, 5.77.

Synthesis of $Pt(O_2CPh)_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (3). A solution of $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (**2**) (0.041 g, 0.08 mmol) and dibenzoyl peroxide (0.019 g, 0.08 mmol) in acetone (5 mL) was heated to 50 °C and stirred for 90 min. The volume was reduced and pentane added to precipitate a yellow solid, which was washed with pentane and dried in a vacuum. Yield: 0.041 g (68%). ^{1}H NMR (acetone-d_6): δ 8.39 (m, 2H, H2,6-Ph_{eq}), 7.90 ('d', 4H, ^{3}J = 7.2 Hz, H2,6-Ph_{ax}), 7.5−7.4 (m, 5H, H3,4,5-Ph_{eq} and H4-Ph_{ax}), 7.31 ('t', 4H, $^{3}J_{Pt-H}$ = 7.2 Hz, H3,5-Ph_{ax}), 7.13 (dd, 1H, ^{3}J = 8.4 Hz and 6.3 Hz, H4-NCN), 7.04 (2, 2H, ^{3}J = 7.8 Hz, H3-NCN), 4.45 (s, 4H, $^{3}J_{Pt-H}$ = 28 Hz, NCH_2), 3.05 (s, 12H, $^{3}J_{Pt-H}$ = 25 Hz, NMe). LSIMS (in mnba): *m/z* 749.4 ($[M]^+$, <1%), 628.3 ($[M - PhCO_2]^+$, 100%), ($[M - 2PhCO_2]^+$, 18%), 385.2 ($[M - H - 3PhCO_2]^+$, 50%). Anal. Calcd for **3**·H_2O: C, 51.61; H, 4.73; N, 3.65. Found: C, 51.81; H, 4.56; N, 3.51.

Synthesis of $PtTol(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (4). Freshly prepared 4-tolyllithium (0.025 g, 2.5 mmol) was dissolved in dry diethyl ether (3 mL) and filtered under an inert atmosphere into a cooled (−78 °C) suspension of $PtCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (0.25 g, 0.59 mmol) in dry diethyl ether (10 mL). The suspension was stirred at low temperature for 20 min, then at ambient temperature for 2 h. The solvent was removed in a vacuum, dichloromethane added, and the suspension filtered through Celite. The volume of the filtrate was reduced and pentane added to give an off-white solid. The solid was collected, washed with diethyl ether, and dried in a vacuum. Yield: 0.18 g (62%). Characterization was as reported by Terheijden et al.[19]

Synthesis of *cis*-$Pt(O_2CPh)_2Tol(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (5). To a solution of crude *cis*-$PtI_2Tol(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ [prepared from the reaction of $PtTol(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (**4**) (0.012 g, 0.025 mmol) and iodine (0.006 g, 0.024 mmol) in benzene] in CH_2Cl_2 (3 mL) was added silver benzoate (0.014 g, 0.061 mmol). The suspension was stirred overnight in the absence of light, filtered through Celite, and evaporated to dryness to give a white solid. The solid was dissolved in a minimum of acetone, and a colorless crystalline solid formed within 24 h in low yield (20%). ^{1}H NMR (acetone-d_6): δ 8.34 (m, 2H, *o-H* PtO_2CPh), 8.21 (dd, 1H, ^{3}J = 8.4 Hz, ^{4}J = 2.2 Hz, $^{3}J_{Pt-H}$ = 29 Hz, H6-Tol), 7.94 (dd, 2H, ^{3}J = 8.0 Hz, ^{4}J = 1.6 Hz, H2,6-Ph′), 7.5−7.4 (m, 3H, H3,4,5-Ph), 7.32−7.26 (m, 2H, H4-Ph′ and H4-NCN), 7.18 (t, 2H, ^{3}J = 7.2 Hz, H3,5-Ph′), 7.05 (d, 2H, ^{3}J = 7.6 Hz, H3,5-NCN), 6.92 (dd, 1H, ^{3}J = 8.4 Hz, ^{4}J = 2.3 Hz, H5-Tol), 6.67 (dd, 1H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, H3-Tol), 6.11 (dd, 1H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, $^{3}J_{Pt-H}$ = 40 Hz H2-Tol), 4.30 (d, 2H, ^{2}J = 14.6 Hz, $^{3}J_{Pt-H}$ = 38 Hz, NCH_2), 4.15 (d, 2H, ^{2}J = 14.6 Hz, $^{3}J_{Pt-H}$ = 33 Hz, NCH_2), 3.11 (s, 6H, $^{3}J_{Pt-H}$ = 25 Hz, NMe), 2.60 (s, 6H, $^{3}J_{Pt-H}$ = 39 Hz, NMe), 2.25 (s, 3H, Me-Tol). Anal. Calcd: C, 55.07; H, 5.04; N, 3.89. Found: C, 54.85; H, 4.78; N, 3.82.

Synthesis of *cis*-$Pt(O_2CPh)_2Me(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (7). Iodomethane (12 μL, 0.19 mmol) was added to a suspension of $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (**2**) (0.010 g, 0.020 mmol) and silver benzoate (0.045 g, 0.20 mmol) in acetone (3 mL). The suspension was stirred at overnight in the absence of light, then filtered through Celite. The filtrate was concentrated in vacuo and pentane added to precipitate the product. The resulting white precipitate was isolated, rinsed with pentane (3 × 1 mL), and dried in vacuo. Yield: 0.009 g (71%). ^{1}H NMR (acetone-d_6): δ 8.27 (dd, 2H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, H2,6-Ph), 7.99 (dd, 2H, ^{3}J = 8.0 Hz, ^{4}J = 1.6 Hz, H2,6-Ph′), 7.42 (m, 3H, H3,4,5-Ph), 7.33 (tt, 1H, ^{3}J = 6.0 Hz, ^{4}J = 1.2 Hz, H4-Ph′), 7.27 (t, 2H, ^{3}J = 7.2 Hz, H3,5-Ph′), 7.09 (dd, 1H, *J* = 8.4 Hz and *J* = 6.8 Hz, H4-NCN), 6.99 (d, 2H, ^{3}J = 7.6 Hz, H3,5-NCN), 4.47 (d, 2H, ^{2}J = 14.4 Hz, $^{3}J_{Pt-H}$ = 36 Hz, NCH_2), 4.34 (d, 2H, ^{2}J = 14.4 Hz, $^{3}J_{Pt-H}$ = 34 Hz, NCH_2), 3.10 (s, 6H, $^{3}J_{Pt-H}$ = 26 Hz, NMe), 2.94 (s, 6H, $^{3}J_{Pt-H}$ = 36 Hz, NMe), 1.62 (s, 3H, $^{3}J_{Pt-H}$ = 70 Hz, Me). LSIMS (in mnba): *m/z* 642.2 ($[M - H]^+$, <1%), 522.2 ($[M - PhCO_2]^+$, 75%), ($[M - H - 2PhCO_2 - Me]^+$, 100%). Anal. Calcd: C, 50.38; H, 5.01; N, 4.35. Found: C, 50.18; H, 4.98; N, 4.27.

^{1}H NMR Studies. Reaction of Dibenzoyl Peroxide with $Pd(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (1). A solution of dibenzoylperoxide (0.0031 g, 7.4 μmol) and **1** (0.0018 g, 7.4 μmol) in acetone-d_6 was allowed to react for several days at ambient temperature with monitoring by ^{1}H NMR. No reaction was observed.

Reaction of Dibenzoyl Peroxide with $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (2). A clear, colorless solution of dibenzoylperoxide (0.009 g, 37 μmol) and **2** (0.015 g, 30 μmol) in $CDCl_3$ was allowed to react for 2 h at 50 °C to give a clear yellow solution. Products were identified by ^{1}H NMR as **3** and benzoic acid (from the decomposition of excess dibenzoylperoxide).

Reaction of Dibenzoyl Peroxide with $Pt(Tol)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (4). A solution of dibenzoyl peroxide (0.0017 g, 0.0070 mmol) in dry CD_2Cl_2 (0.4 mL) was added to a solution of $PtTol(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (**4**) (0.0035 g, 0.0073 mmol) in CD_2Cl_2 (0.3 mL). The reaction was monitored by ^{1}H NMR spectroscopy at room temperature over several days.

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Table 2. Crystal Data and Details of the Structure Determinations of $M(O_2CPh)(NCN)$ [M = Pd (1), Pt (2)] and Solvates of Complexes 3, 5, and 7: $Pt(O_2CPh)_3(NCN)\cdot 1/2Me_2CO$, $Pt(O_2CPh)_2Tol(NCN)\cdot Me_2CO$, and $Pt(O_2CPh)_2Me(NCN)\cdot Me_2CO\cdot H_2O$, where NCN = [2,6-(Dimethylaminomethyl)phenyl-*N*,*C*,*N*]$^-$

	1	**2**	**3**·1/2Me$_2$CO	**5**·Me$_2$CO	**7**·Me$_2$CO·H$_2$O
formula	$C_{19}H_{24}N_2O_2Pd$	$C_{19}H_{24}N_2O_2Pt$	$C_{34.5}H_{37}N_2O_{6.5}Pt$	$C_{36}H_{42}N_2O_5Pt$	$C_{30}H_{40}N_2O_6Pt$
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)	$C2/c$ (C_{2h}^6, No. 15)	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/n$ (C_{2h}^5, No. 14 (variant))
a/Å	8.9377(5)	8.9088(8)	13.0359(8)	11.8427(8)	9.3107(7)
b/Å	9.9806(6)	10.0224(8)	30.474(2)	12.6435(8)	11.6368(9)
c/Å	11.1160(6)	11.1315(9)	8.9499(6)	12.8944(8)	27.094(2)
α/deg	110.956(1)	110.808(2)		100.580(2)	
β/deg	102.367(1)	102.223(2)	120.484(2)	114.772(1)	95.497(2)
γ/deg	98.624(1)	98.923(2)		104.139(1)	
V/Å^3	$876._2$	$878._7$	3534	1608	2922
Z	2	2	4	2	4
M_r	418.8	507.5	778.8	777.8	717.7
D_c/g cm^{-3}	1.58_7	1.91_8	1.46_3	1.60_6	1.63_1
dimensions/mm	0.32 × 0.23 × 0.14	0.24 × 0.22 × 0.09	0.20 × 0.14 × 0.07	0.28 × 0.22 × 0.18	0.35 × 0.09 × 0.06
μ_{Mo}/mm^{-1}	1.07	8.0	4.0	4.4	4.9
$2\theta_{max}$/deg	75	75	75	75	65
$T_{min/max}$	0.78	0.49	0.63	0.63	0.71
N_t	18 083	18 095	36 780	33 458	46 630
N	9000	9008	8038	16 522	10 619
N_o	7730	8216	6547	12 566	8242
R_{int}	0.025	0.034	0.060	0.044	0.046
R	0.032	0.025	0.038	0.040	0.049
R_w	0.037	0.031	0.052	0.044	0.072

Reaction of Iodomethane with $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2$-2,6) (2). Complex **2** (0.01 g, 20 μmol) was added to a large excess of iodomethane (1 mL, 16 mmol) at 0 °C. The solution was stirred at 0 °C for 2 h and the solvent removed in a vacuum at low temperature leaving a white residue. The products were identified by ^{1}H NMR at 0 °C as *cis*-$Pt(O_2CPh)_2Me(C_6H_3\{CH_2NMe_2\}_2$-2,6) (**7**) and $PtI(C_6H_3\{CH_2NMe_2\}_2$-2,6) (**6**) and were present in approximately 1:1 ratio. When carried out at ambient temperature over 2 nights, the products, identified by ^{1}H NMR, were **6** and methyl benzoate in a 1:1 ratio along with unreacted iodomethane.

Reaction of Iodomethane, Silver Benzoate, and $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2$-2,6) (2). A suspension of silver benzoate (0.0712 g, 0.311 mmol), iodomethane (19 μL, 0.30 mmol), and **2** (0.0153 g, 0.0301 mmol) in acetone-d_6 (1 mL) was stirred in the absence of light for 24 h. The suspension was filtered through Celite. A ^{1}H NMR of the clear, colorless filtrate was measured immediately. Products were identified as *cis*-$Pt(O_2CPh)_2Me(C_6H_3\{CH_2NMe_2\}_2$-2,6) (**7**), methyl benzoate, and unreacted iodomethane.

Decomposition of *cis*-$Pt(O_2CPh)_2Me(C_6H_3\{CH_2NMe_2\}_2$-2,6) (7). A solution of **7** in acetone-d_6 was heated at 50 °C for 4 h. Decomposition products were present in a 1:1 ratio and were identified by ^{1}H NMR as $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2$-2,6) (**2**) and methyl benzoate.

Reaction of Iodomethane with $Pd(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2$-2,6) (1). Complex **1** (0.002 g, 5 μmol) was added to a large excess of iodomethane-d_3 (0.8 mL). The solution was stirred for several days at ambient temperature. The reaction was monitored by ^{1}H NMR, and after 4 days, the products were identified by ^{1}H NMR and GC−MS (volatile compounds) as $PdI(C_6H_3\{CH_2NMe_2\}_2$-2,6) (**8**) and methyl-d_3 benzoate in a 1:1 ratio. No Pd(IV) intermediates were observed.

Reaction of Iodomethane and Silver Benzoate, with $Pd(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2$-2,6) (1). A suspension of silver benzoate (0.0107 g, 47 μmol), iodomethane (3 μL, 48 μmol), and **1** (0.0018 g, 4.3 μmol) in acetone-d_6 (0.8 mL) was stirred in the absence of light for 24 h. Products were identified by ^{1}H NMR as **1**, methyl benzoate, and unreacted iodomethane.

Reaction of Sodium Iodide and $Pt(O_2CPh)(C_6H_3\{CH_2NMe_2\}_2$-2,6) (2). To a solution of **2** (0.001 g, 20 μmol) in acetone-d_6 (0.8 mL) was added sodium iodide (0.004 g, 27 μmol). The suspension was allowed to react for 30 min, and a ^{1}H NMR was measured. The only visible product was $PtI(C_6H_3\{CH_2NMe_2\}_2$-2,6) (**6**).

X-ray Data Collection, Structure Determination, and Refinement for 1, 2, and Solvated Crystals Containing Molecules of 3, 5, and 7. Crystals of the complexes were obtained by the vapor diffusion of pentane into solutions of **1**−**3** or **5** at ambient temperature, and **7** at −20 °C. Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K), yielding N_t total reflections, merging to N unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered "observed" and used in the full-matrix least-squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ are cited at convergence [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[36] Pertinent results are given in the tables and figures, the latter showing 50% probability displacement amplitudes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Variata. In complex **3**·1/2Me$_2$CO, as modeled in space group $C2/c$, the benzoate group trans to the NCN ligand (which lies on the crystallographic 2-axis) is disordered about the axis over two sets of sites of equal occupancy, the difference between the two components of the coordinated oxygen being 0.50(1) Å. Attempted refinement in a lower symmetry space group was not fruitful. For complex **7**·Me$_2$CO·H$_2$O hydrogen atoms were not located in association with the putative water molecule oxygen atom. A substantial difference map residue (9 e Å^{-3}) was located 0.7 Å from the metal atom, suggesting, for example, possible cocrystallization of a minor related impurity or disorder.

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Supporting Information Available: Tables of atom coordinates, displacement parameters, and bond distances and angles for **1**, **2**, **3**·1/2Me$_2$CO, **5**·Me$_2$CO, and **7**·Me$_2$CO·H$_2$O; kinetic data for decomposition of complex **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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