Carbon−Oxygen Bond Formation at Organopalladium Centers: The Reactions of $PdMeR(L_2)$ (R = Me, 4-tolyl; L_2 = tmeda, bpy) with Diaroyl Peroxides and the Involvement of Organopalladium(IV) Species

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The group 16 oxidants dibenzoyl- and bis(4-trifluoromethylbenzoyl)-peroxide react with dimethylpalladium(II) and methyl(4-tolyl)palladium(II) complexes of the bidentate nitrogen donor ligands 2,2′-bipyridine and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in discrete stepwise processes as the temperature is raised from −70 °C. Carbon−oxygen bonds are formed during this reaction sequence but not from those Pd(IV) complexes detected spectroscopically. The initial reaction gives undetected "$Pd^{IV}(O_2CAr)_2MeR(L_2)$" (Ar = Ph, Ar_F; R = Me, Tol; L_2 = bpy, tmeda), which immediately undergo methyl aroate exchange with $Pd^{II}MeR(L_2)$ to give $Pd^{II}(O_2CAr)R(L_2)$ and $Pd^{IV}(O_2CAr)Me_2R(L_2)$, where all products except for $Pd^{IV}(O_2CAr)Me_2$-Tol(tmeda) were detected by ^1H NMR spectroscopy. On raising the temperature, the Pd^{IV}-Me_3 complexes reductively eliminate Me−Me, and the $Pd^{IV}Me_2Tol$ complexes eliminate Me−Me and Tol−Me. The resultant Pd(II) complexes $Pd^{II}(O_2CAr)R(L_2)$ react with $(ArCO_2)_2$ at higher temperatures to form $Pd^{II}(O_2CAr)_2(L_2)$ and R-O_2CAr (R = Me, Tol), except for $Pd^{II}(O_2$-CAr)Tol(tmeda), which forms $Pd^{II}(O_2CAr)_2$(tmeda) and 4,4′-bitolyl. Each reaction step has been confirmed by the independent synthesis of intermediates $Pd^{II}(O_2CAr)_2(L_2)$ and $Pd^{II}(O_2$-CAr)$R(L_2)$ (Ar = Ph, Ar_F; R = Me, Tol; L_2 = bpy, tmeda) and $Pd^{IV}(O_2CR)Me_2R(L_2)$ (R = Ph, Ar_F; R = Me, Tol; L_2 = bpy) by metathesis reactions of halogeno complexes with Ag[O_2CAr], followed by temperature-dependent studies of both the decomposition of Pd(IV) complexes and reactions of Pd(II) complexes with $(ArCO_2)_2$. Attempts to prepare "$Pd^{IV}(O_2CAr)_2MeR$-(bpy)" in a similar manner (and thus in the absence of PdMeR(bpy) with which they undergo exchange reactions) were unsuccessful, but the complexes $Pd^{IV}I_2MeR$(bpy) (R = Me, Tol) that formed on reaction of diiodine with $PdMeR(L_2)$ were detected and found to reductively eliminate iodomethane. X-ray structural studies are reported for the square-planar palladium(II) complexes $Pd(O_2CPh)_2$(bpy), $Pd(O_2CAr)_2$(tmeda) (Ar = Ph, Ar_F), and Pd(O_2CPh)-(Tol)(bpy)·CH_2Cl_2.

Introduction

Carbon−oxygen bond formation at palladium centers is an important process currently attracting considerable attention. Although much of this interest has focused on coupling occurring from Pd(II) centers,[1] organopalladium(IV) species have been postulated as intermediates in a variety of processes including the acetoxylation of arenes (eq 1)[2] and the formation of carbon−oxygen bonds in the reaction of organopalladium(II) complexes with oxygen-atom-containing oxidizing agents such as 3-chloroperbenzoic acid,[3] *tert*-butylhydroperoxide,[4] molybdenum peroxides,[5] and hypervalent iodine(III) reagents.[3g,h,6] However, the suggested intermediates have yet to be detected spectroscopically. In contrast, the intermediacy of Pd(IV) has been detected for closely related carbon−selenium coupling, the first demonstrated model reaction for carbon−heteroatom (group 16) coupling at Pd(IV). Crystalline *trans*-

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$Pd(SePh)_2Me_2(bpy)$ (bpy = 2,2′-bipyridine) has been isolated from the reaction of $PdMe_2(bpy)$ with diphenyl diselenide and characterized by X-ray crystallography. When redissolved in $CDCl_3$, this complex decomposes, resulting in the formation of carbon−carbon bonds (Me−Me) and carbon−selenium bonds (Me−SePh) in ∼1:1 ratio, together with Pd(II) products (eq 2).[7]

$$\text{arene} \xrightarrow[\text{oxidant}]{MeCO_2H/Pd(O_2CMe)_2} \text{Ar-}O_2CMe \qquad (1)$$

$$Pd^{II}Me_2(bpy) + (PhSe)_2 \rightarrow Pd^{IV}(SePh)_2Me_2(bpy) \rightarrow \sim 0.5\ Me{-}Me + \sim 0.5\ Me{-}SePh \qquad (2)$$

Both carbon−carbon and carbon−oxygen coupling have been directly observed in reductive elimination from triorganoplatinum(IV) complexes of the form *fac*-$Pt(OR)Me_3L_2$ [L_2 = 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)benzene; OR = O_2CMe, O_2CCF_3, OTol-4; L = PMe_3, OR = OTol-4].[8] In each case, reductive elimination occurs by preliminary dissociation of a ligand (OR^- in the case of carbon−oxygen coupling, and OR^- or unidentate phosphine in the case of carbon−carbon coupling) to give a five-coordinate intermediate. This is followed by either nucleophilic attack by OR^- on a Pt(IV)-bound methyl group to give Me-OR, or carbon−carbon coupling from the five-coordinate species to give ethane. The selectivity of this reaction has been demonstrated to be highly solvent dependent.

In view of the success in detecting C−Se coupling from Pd(IV) (eq 2), where the Pd(IV) species is formed using diphenyl diselenide as an oxidant, the reactivity of $PdMe_2(bpy)$ toward dibenzoyl peroxide was investigated showing that, along with Pd(II) products, ethane, Me-O_2CPh, and $PhCO_2H$ (upon workup) were formed.[7] This reaction was assumed to proceed via an intermediate of the form "$PdMe_2(O_2CPh)_2(bpy)$",[7] related to eq 2 and to stable Pt(IV) complexes formed on oxidative addition of $(PhCO_2)_2$ to dimethyl- and diaryl-platinum(II) complexes.[9] A detailed analysis of this and related reaction systems is reported here, showing that Pd(IV) intermediates are involved and that methyl group exchange reactions occur between Pd(II) and Pd(IV) centers, but that C−O coupling does not occur from the proposed diorganopalladium(IV) intermediate or from a detected triorganopalladium(IV) intermediate. Arylpalladium(II) substrates have been included in this study in an attempt to detect $C(sp^2)$−O coupling from species containing carboxylate ligands coordinated to arylpalladium(IV) and in an attempt to model proposed intermediates in the catalysis shown in eq 1. Structural studies of Pd(II) products and a Pd(II) intermediate complex are presented, together with an assessment of the potential involvement of Pd(IV) species in carbon−oxygen coupling processes. A preliminary communication of part of this work has appeared.[10]

Scheme 1. Reaction of a 2:3 Ratio of $Pd^{II}Me_2(L_2)$ (L_2 = bpy, tmeda) and $(ArCO_2)_2$ (Ar = Ph, Ar_F) in Acetone-d_6 or CD_2Cl_2

(i) Up to ∼ -30 °C (Ar = Ph and Ar_F):

$$Pd^{II}Me_2(L_2) + (ArCO_2)_2 \rightarrow \underset{\mathbf{A}}{\text{"}Pd^{IV}(O_2CAr)_2Me_2(L_2)\text{"}} \qquad (3)$$

$$Pd^{II}Me_2(L_2) + \underset{\mathbf{A}}{\text{"}Pd^{IV}(O_2CAr)_2Me_2(L_2)\text{"}} \rightarrow \underset{\mathbf{1\text{-}4}}{Pd^{IV}(O_2CAr)Me_3(L_2)} + \underset{\mathbf{5\text{-}8}}{Pd^{II}(O_2CAr)Me(L_2)} \qquad (4)$$

(ii) Above ∼ -30 °C (Ar = Ph and Ar_F):

$$\underset{\mathbf{1\text{-}4}}{Pd^{IV}(O_2CAr)Me_3(L_2)} \rightarrow \underset{\mathbf{5\text{-}8}}{Pd^{II}(O_2CAr)Me(L_2)} + Me\text{-}Me \qquad (5)$$

(iii) Above ∼ -10 °C (Ar = Ph; L_2 = bpy); Above ∼ -20 °C (Ar = Ph; L_2 = tmeda); Above ∼ -30 °C (Ar = Ar_F; L_2 = bpy, tmeda):

$$\underset{\mathbf{5\text{-}8}}{Pd^{II}(O_2CAr)Me(L_2)} + (ArCO_2)_2 \rightarrow \underset{\mathbf{9\text{-}12}}{Pd^{II}(O_2CAr)_2(L_2)} + Me\text{-}O_2CAr \qquad (6)$$

(iv) Overall reaction

$$2\ Pd^{II}Me_2(L_2) + 3\ (ArCO_2)_2 \rightarrow \underset{\mathbf{9\text{-}12}}{2\ Pd^{II}(O_2CAr)_2(L_2)} + 2\ Me\text{-}O_2CAr + Me\text{-}Me \qquad (7)$$

Results and Discussion

The reactivity of PdMeR(bpy) complexes toward diaroyl peroxides was monitored by ^1H NMR spectroscopy. Addition of a solution of the peroxide in acetone-d_6 or CD_2Cl_2 to the complex at low temperature (< −50 °C), followed by slow warming, allowed the elucidation of a complicated series of reactions leading to the products observed at ambient temperature. Studies were initially confined to the reaction of $PdMe_2(bpy)$ with $(PhCO_2)_2$. Investigations were then extended to include methyl(aryl)palladium systems, for which less stable Pd(IV) species would be anticipated, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) as an aliphatic and more flexible ligand than bpy. Solubility difficulties led to the use of bis(4-trifluoromethylbenzoyl) peroxide, $(Ar_FCO_2)_2$, to enhance the solubility of intermediates and end-products.

^1H NMR Studies of the Reaction of $PdMe_2(L_2)$ (L_2 = bpy, tmeda) with $(ArCO_2)_2$ (Ar = Ph, Ar_F). Variable-temperature ^1H NMR studies of the reaction of $PdMe_2(bpy)$ with $(PhCO_2)_2$ revealed a complex series of reactions, which proceed in the same manner in both acetone-d_6 and CD_2Cl_2. Several mole ratios of reagents were explored, and it was found that only in the case of a $2PdMe_2(L_2)$:$3(ArCO_2)_2$ ratio did the reaction proceed to completion with full consumption of both reagents. At temperatures below −30 °C $PdMe_2(bpy)$ and $(PhCO_2)_2$ reacted slowly to form $Pd(O_2CPh)Me_3(bpy)$ (**1**) and $Pd(O_2CPh)Me(bpy)$ (**5**). The proposed intermediacy of "$Pd(O_2CAr)_2Me_2(L_2)$" (**A**, eq 3 in Scheme 1) and the subsequent exchange reactions (eq 4) are discussed below. Warming to −30 °C led to a decrease in **1**,

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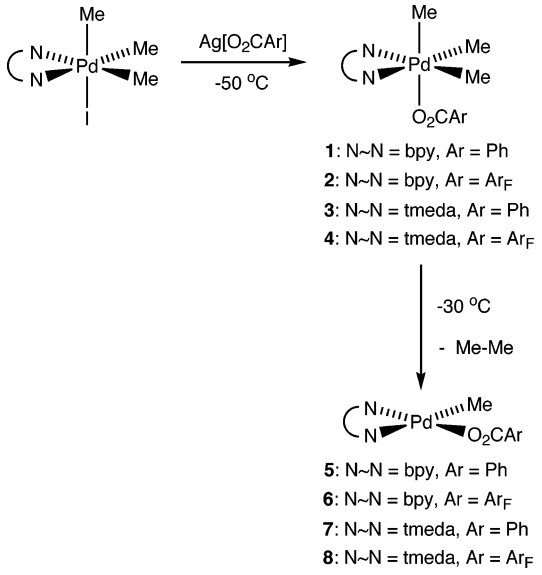
accompanied by an increase in the amount of **5** and the formation of ethane (eq 5). At −10 °C, **5** decreased and the formation of Me-O_2CPh along with the precipitation of a yellow crystalline solid was observed (eq 6), resulting in the overall reaction shown in eq 7. X-ray crystallographic studies confirmed the identity of the solid as $Pd(O_2CPh)_2(bpy)$ (**9**). An identical reaction sequence was observed for the reaction of $PdMe_2(bpy)$ with $(Ar_FCO_2)_2$, although C−O coupling to form Me-O_2CAr_F (eq 6) occurred at a lower temperature (−30 °C). Unlike **9**, the inorganic product, $Pd(O_2CAr_F)_2(bpy)$ (**10**), was soluble, allowing the stoichiometry of the reaction to be determined. Complex **10** and Me-O_2CAr_F were present in equal amounts, but ethane could not be quantified reliably by NMR due to its volatility.

The reaction of $PdMe_2(tmeda)$ with $(ArCO_2)_2$ (R = Ph, Ar_F) followed an identical series of reactions with analogous intermediates identified at similar temperatures. The inorganic product $Pd(O_2CAr_F)_2(tmeda)$ (**12**) and $Pd(O_2CPh)_2(tmeda)$ (**11**) were soluble, allowing the product ratio $Pd(O_2CAr)_2(tmeda)$:Me-O_2CPh to be determined as 1:1. As seen in the reaction of the bpy complexes, the formation Me-O_2CAr_F was observed at a lower temperature than Me-O_2CPh (eq 6).

The proposed sequence of eqs 3−6 was studied in detail by carrying out a series of specific reactions. Reagents were mixed in different ratios and held at different temperatures in order to halt the reaction sequence at different stages. The specific reactions proceeded at temperatures identical to those of related reactions in Scheme 1. Thus, when the reagents $PdMe_2(L_2)$ and $(PhCO_2)_2$ were mixed in a 2:1 ratio and the reaction allowed to go to completion below −30 °C, $Pd(O_2CPh)Me_3(L_2)$ (**1**, **3**) and $Pd(O_2CPh)Me(L_2)$ (**5**, **7**) were observed in ∼1:1 ratio with no reagents remaining, in agreement with eqs 3 and 4. In the case where L_2 = bpy with the reaction carried out in acetone-d_6, $Pd(O_2CPh)Me(bpy)$ (**5**) gradually precipitated at low temperature, generating uncertainty in the accuracy of the observed product ratio, but this limitation was overcome by performing the reaction in CD_2Cl_2. Warming to temperatures above −30 °C led to the decomposition of $Pd(O_2CPh)Me_3(L_2)$ (**1**, **3**) (eq 5), with $Pd(O_2CPh)Me(L_2)$ (**5**, **7**) and ethane the only species observed at the completion of the reaction. Undetected "$Pd^{IV}(O_2CPh)_2Me_2(L_2)$" (**A**) is assumed to undergo the exchange reaction shown in eq 4. Such reactions are often observed in Pd(IV) chemistry on reaction of triorganopalladium(IV) complexes with diorganoplatinum(II)[11a] and diorganopalladium(II) substrates.[11b,c]

Some of the intermediates were synthesized independently and their proposed reactions investigated. The reactions of eq 5 were investigated by the in situ preparation of the Pd(IV) intermediates $Pd(O_2CAr)Me_3(L_2)$ (**1**−**4**) from $PdIMe_3(L_2)$ and Ag[O_2CAr] at −50 °C in acetone-d_6 (Scheme 2). Decomposition to $Pd(O_2CAr)Me(L_2)$ (**5**−**8**) and ethane was observed at ca. −30 °C. The independent syntheses of $Pd(O_2CAr)Me(L_2)$ (**5**−**8**) from $PdIMe(L_2)$ and Ag[O_2CAr] confirmed their identity as intermediates, and their reactions with $(ArCO_2)_2$ proceeded as shown by eq 6.

Scheme 2. Synthesis and Decomposition of Unstable Trimethylpalladium(IV) Complexes in Acetone-d_6



^{1}H NMR Studies of the Reaction of PdMeTol(bpy) (Tol = 4-tolyl) and $(ArCO_2)_2$ (Ar = Ph, Ar_F). The reaction of PdMeTol(bpy) with $(PhCO_2)_2$ displayed close similarities to eqs 3−7 (Scheme 3). When $(PhCO_2)_2$ was added to PdMeTol(bpy) at temperatures below −30 °C in acetone-d_6, a slow reaction to form $Pd(O_2CPh)Me_2Tol(bpy)$ (**13**) and $Pd(O_2CPh)Tol(bpy)$ (**15**) was observed. On warming to −30 °C, the quantity of **13** observed decreased and $Pd(O_2CPh)Me(bpy)$ (**5**), $Pd(O_2CPh)Tol(bpy)$ (**15**), 1,4-xylene (Tol-Me), and ethane were detected. At −10 °C, the appearance of Me-O_2CPh and $Pd(O_2CPh)_2(bpy)$ (**9**) was accompanied by a decrease in **5**. Further warming to ambient temperature led to the very slow appearance of Tol-O_2CPh along with an increase in **9** and the slow disappearance of **15**. These observations are consistent with the reaction sequence shown in eqs 8−12 to give the overall reaction in eq 13, where n = 0.6. Using $(Ar_FCO_2)_2$ as the oxidant, a different product ratio was observed for Tol−Me and Me−Me coupling in eq 10 to give n = 0.4. In several of the specific reactions, 4,4′-bitolyl was observed as a minor product. Its presence predominantly occurred in reactions carried out entirely at room temperature and was largely suppressed in reactions performed at low temperature. The formation of biaryls as a product in palladium-mediated reactions is common, and several mechanisms for their formation have been proposed.[12]

When the reagents PdMeTol(bpy) and $(ArCO_2)_2$ were mixed in a 2:1 ratio in acetone-d_6 and the reaction was allowed to go to completion at −40 °C, all reagents were consumed and $Pd(O_2CAr)Me_2Tol(bpy)$ (**13**, **14**; isomers illustrated in Scheme 4) and $Pd(O_2CAr)Tol(bpy)$ (**15**, **16**) were observed in 1:1 ratio, in accord with eqs 8 and 9. The ratio of Pd(IV) isomers depended on the solvent

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Scheme 3. Reaction of $Pd^{II}MeTol(bpy)$ with $(ArCO_2)_2$ (Ar = Ph, Ar_F) in 2:3 Ratio in Acetone-d_6 or CD_2Cl_2

(i) Up to ~ -30 °C:

$$Pd^{II}MeTol(bpy) + (ArCO_2)_2 \rightarrow \underset{\mathbf{B}}{\text{"}Pd^{IV}(O_2CAr)_2MeTol(bpy)\text{"}} \quad (8)$$

$$Pd^{II}MeTol(bpy) + \underset{\mathbf{B}}{\text{"}Pd^{IV}(O_2CAr)_2MeTol(bpy)\text{"}} \rightarrow \underset{\mathbf{13, 14}}{Pd^{IV}(O_2CAr)Me_2Tol(bpy)} + \underset{\mathbf{15, 16}}{Pd^{II}(O_2CAr)Tol(bpy)} \quad (9)$$

(ii) Above ~ -30 °C:

$$\underset{\mathbf{13, 14}}{Pd^{IV}(O_2CAr)Me_2Tol(bpy)} \rightarrow n\ \underset{\mathbf{5, 6}}{Pd^{II}(O_2CAr)Me(bpy)} + n\ \text{Tol-Me} + (1-n)\ \underset{\mathbf{15, 16}}{Pd^{II}(O_2CAr)Tol(bpy)} + (1-n)\ \text{Me-Me} \quad (10)$$

(iii) Above ~ -10 °C:

$$n\ \underset{\mathbf{5, 6}}{Pd^{II}(O_2CAr)Me(bpy)} + n\ (ArCO_2)_2 \rightarrow n\ \underset{\mathbf{9, 10}}{Pd^{II}(O_2CAr)_2(bpy)} + n\ \text{Me-}O_2CAr \quad (11)$$

(iv) Room temperature:

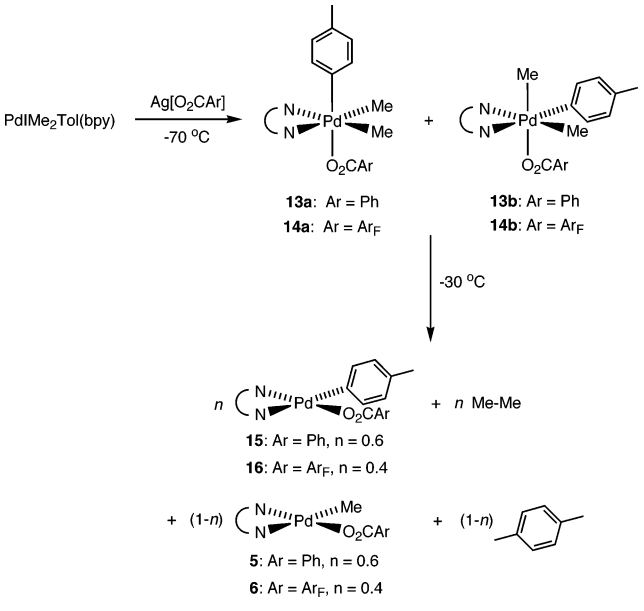
$$(2-n)\ \underset{\mathbf{15, 16}}{Pd^{II}(O_2CAr)Tol(bpy)} + (2-n)\ (ArCO_2)_2 \rightarrow (2-n)\ \underset{\mathbf{9, 10}}{Pd^{II}(O_2CAr)_2(bpy)} + (2-n)\ \text{Tol-}O_2CAr \quad (12)$$

(v) Overall reaction:

$$2\ Pd^{II}MeTol(bpy) + 3\ (ArCO_2)_2 \rightarrow 2\ \underset{\mathbf{9, 10}}{Pd^{II}(O_2CAr)_2(bpy)} + (2-n)\ \text{Tol-}O_2CAr + n\ \text{Tol-Me} + n\ \text{Me-}O_2CAr + (1-n)\ \text{Me-Me} \quad (13)$$

Ar = Ph: $n = 0.6$; Ar = Ar_F: $n = 0.4$.

Scheme 4. Synthesis and Decomposition of Dimethyl(tolyl)(2,2′-bipyridine)palladium(IV) Complexes in Acetone-d_6



Ratio **13a**:**13b** = **14a**:**14b** = 1:1

used but not on the choice of oxidant. In acetone-d_6 a 1:1 ratio of isomers was seen, while in CD_2Cl_2 a 1:2 ratio was observed.

To model eq 10 and to confirm the identity of the observed Pd(IV) intermediates (**13**, **14**), $PdIMe_2Tol(bpy)$ was reacted with $Ag[O_2CAr]$ at −70 °C in an NMR tube (Scheme 4). ^1H NMR spectroscopy confirmed the presence of the above as two isomers, $Pd^{IV}(O_2CAr)Me_2Tol(bpy)$ (**13**, **14**), which persisted to ca. −30 °C, at which temperature they decomposed to give the products according to eq 10. Independently synthesized $Pd(O_2CAr)Tol(bpy)$ (**15**, **16**) was shown to react with $(ArCO_2)_2$ very slowly at ambient temperature to form $Tol\text{-}O_2CAr$ and $Pd(O_2CAr)_2(bpy)$ (**9**, **10**), in agreement with eq 12.

^1H NMR Studies of the Reaction of PdMeTol(tmeda) (Tol = 4-tolyl) with $(ArCO_2)_2$ (Ar = Ph, Ar_F). In view of the results obtained for the bpy systems, reactions of PdMeTol(tmeda) with $(ArCO_2)_2$ were initially studied in a 2:3 ratio in acetone-d_6. No reaction was observed until > −30 °C (Ar = Ph) or −50 °C (Ar = Ar_F), when $Pd(O_2CAr)Me(tmeda)$ (**7**, **8**), $Pd(O_2CAr)Tol(tmeda)$ (**17**, **18**), 1,4-Tol-Me, and ethane began to form (Scheme 5). No Pd(IV) intermediates were observed. Warming to > −20 °C (Ar = Ph) or −30 °C (Ar = Ar_F) led to the appearance of $Pd(O_2CAr)_2(tmeda)$ (**11**, **12**) and $Me\text{-}O_2CAr$ and a decreased amount of $Pd(O_2CAr)Me(tmeda)$ (**7**, **8**). At ambient temperature, the reaction continued over several days, forming 4,4′-bitolyl and further $Pd(O_2CAr)_2(tmeda)$ (**11**, **12**), while $Pd(O_2CAr)Tol(tmeda)$ (**17**, **18**) decreased. The final products, after several days at ambient temperature, were $Pd(O_2CAr)_2(tmeda)$ (**11**, **12**), 1,4-Tol-Me, $Me\text{-}O_2CAr$, and 4,4′-Tol_2, with the notable absence of $Tol\text{-}O_2CAr$. Not all of the peroxide was consumed in these reactions.

On the basis of results for the bpy systems, these reactions are anticipated to proceed as shown in eqs 14−17. Unlike $Pd(O_2CAr)Tol(bpy)$ (**15**, **16**), which react with

Scheme 5. Reaction of $Pd^{II}MeTol(tmeda)$ with $(ArCO_2)_2$ (Ar = Ph, Ar_F) in Acetone-d_6

(i) Above ~ -30 °C (Ar = Ph); Above ~ -50 °C (Ar = Ar_F):

$$Pd^{II}MeTol(tmeda) + (ArCO_2)_2 \rightarrow \underset{\mathbf{C}}{"Pd^{IV}(O_2CAr)_2MeTol(tmeda)"} \quad (14)$$

$$Pd^{II}MeTol(tmeda) + \underset{\mathbf{C}}{"Pd^{IV}(O_2CAr)_2MeTol(tmeda)"} \rightarrow \underset{\mathbf{D}}{"Pd^{IV}(O_2CAr)Me_2Tol(tmeda)"} + \underset{\mathbf{17, 18}}{Pd^{II}(O_2CAr)Tol(tmeda)} \quad (15)$$

$$\underset{\mathbf{D}}{"Pd^{IV}(O_2CAr)Me_2Tol(tmeda)"} \rightarrow \underset{\mathbf{7, 8}}{n\ Pd^{II}(O_2CAr)Me(tmeda)} + n\ Tol\text{-}Me + \underset{\mathbf{17, 18}}{(1\text{-}n)\ Pd^{II}(O_2CAr)Tol(tmeda)} + (1\text{-}n)\ Me\text{-}Me \quad (16)$$

(iii) Above ~ -20 °C (Ar = Ph); Above ~ -30 °C (Ar = Ar_F):

$$\underset{\mathbf{7, 8}}{n\ Pd^{II}(O_2CAr)Me(tmeda)} + n\ (ArCO_2)_2 \rightarrow \underset{\mathbf{11, 12}}{n\ Pd^{II}(O_2CAr)_2(tmeda)} + n\ Me\text{-}O_2CAr \quad (17)$$

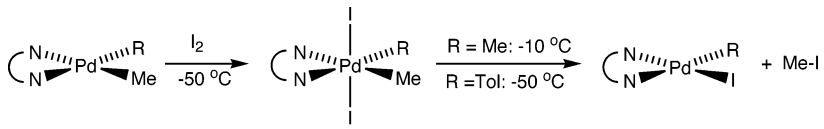
(iv) Room temperature:

$$(2\text{-}n)\ \underset{\mathbf{17, 18}}{Pd^{II}(O_2CAr)Tol(tmeda)} + (2\text{-}n)/2\ (ArCO_2)_2 \rightarrow \underset{\mathbf{11, 12}}{(2\text{-}n)Pd^{II}(O_2CAr)_2(tmeda)} + (2\text{-}n)/2Tol\text{-}Tol \quad (18)$$

(v) Overall reaction:

$$2\ Pd^{II}MeTol(tmeda) + (2 + n/2)\ (ArCO_2)_2 \rightarrow \underset{\mathbf{11, 12}}{2\ Pd^{II}(O_2CAr)_2(tmeda)} + (1\text{-}n)\ Me\text{-}Me + n\ Tol\text{-}Me + n\ Me\text{-}O_2CAr + (2\text{-}n)/2\ Tol\text{-}Tol \quad (19)$$

Scheme 6. Synthesis and Decomposition of $PdI_2MeR(bpy)$ Complexes in Acetone-d_6



19: N~N = bpy, R = Me

20: N~N = bpy, R = Tol

1 equiv of $(ArCO_2)_2$, $Pd(O_2CAr)Tol(tmeda)$ (**17**, **18**) react with only half an equivalent of $(ArCO_2)_2$, as shown in eq 18. Consequently, the overall stoichiometry for complete consumption of reagents would not be a 2:3 ratio, but rather would require a reagent ratio of 2:{(1 + *n*) + [(2 − *n*)/2]} = 2:[2 + (*n*/2)] (from eqs 14−18). To determine the stoichiometry of the reaction, *n* would need to be determined from the product distribution of eq 16, but this proved to be very difficult owing to some competition, even at low temperature, between the reactions of eq 16 and $Pd(O_2CAr)Me(tmeda)$ (**7**, **8**) with $(ArCO_2)_2$ (eq 17). In addition, $PdIMe_2Ph(tmeda)$ is too unstable to be observed,[11b] and thus specific reactions using "$Pd(O_2CAr)Me_2Tol(tmeda)$" (**D**) were not considered feasible. The independently prepared complexes $Pd(O_2CAr)Tol(tmeda)$ (**17**, **18**) reacted slowly with diaroyl peroxide at ambient temperature to form $Pd(O_2CAr)_2(tmeda)$ (**11**, **12**) and 4,4′-bitolyl (eq 18), but no $Tol\text{-}O_2CAr$ was formed.

Synthesis and Decomposition of $PdI_2MeR(bpy)$ (R = Me, 4-tolyl). It is proposed above that undetected species "$Pd(O_2CAr)_2MeR(L_2)$" react with $PdMeR(L_2)$, as shown in Schemes 1, 3, 5, and 6. It was possible to synthesize $Pd(O_2CAr)Me_2R(L_2)$ (**1**−**4**, **13**, **14**) by metathesis involving $Ag[O_2CAr]$ (Schemes 2 and 4), and so we investigated the reaction of diiodine with PdMeR(bpy) (R = Me, Tol), followed by reaction with $Ag[O_2CPh]$, in an attempt to generate "$Pd(O_2CPh)_2MeR(bpy)$" in the absence of PdMeR(bpy). Reaction with diiodine generated $PdI_2MeR(bpy)$ at low temperature (< −50 °C), where the complexes exhibit ^1H NMR spectra indicating trans oxidative addition of diiodine and the absence of other isomers, e.g., one pyridyl and one PdMe environment for **19**, two pyridyl and one PdMe environment for **20**, the PdMe chemical shifts for **19** (2.75 ppm) and **20** (2.30 ppm) being typical for methyl groups trans to bpy but different from methyl groups trans to iodo groups, e.g., 1.12 ppm for $PdIMe_3(bpy)$.[19] Similar com-

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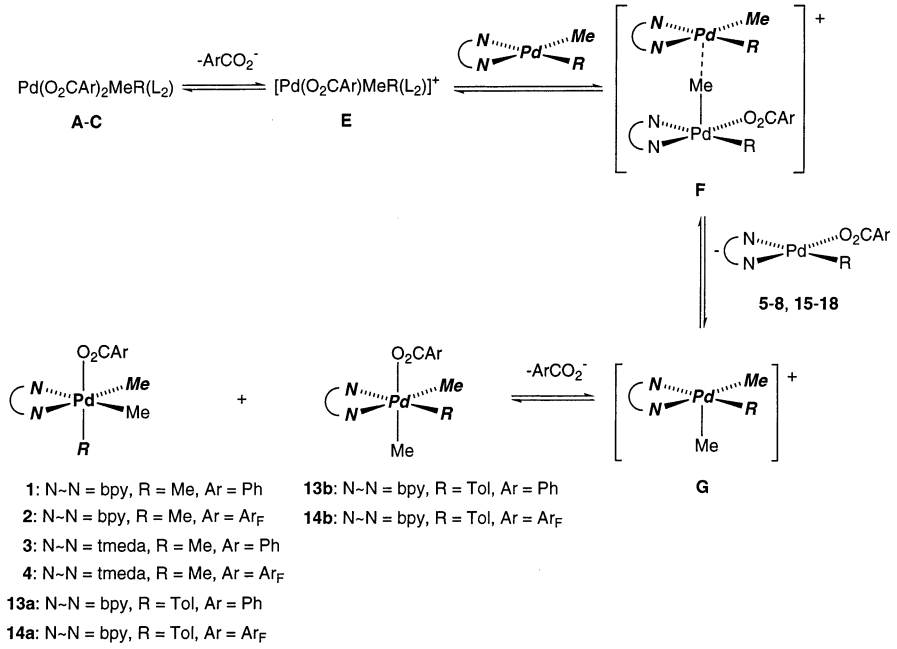
Scheme 7. Exchange Reactions between Unobserved "$Pd(O_2CAr)_2MeR(L_2)$" and $PdMeR(L_2)$



plexes $PdI_2Me_2(L_2)$ [L_2 = bis(4-tolylimino)acenaphthene, bis(phenylimino)camphane][13] have been reported. Complexes **19** and **20** cleanly reductively eliminate iodomethane at ca. −10 °C [R = Me (**19**)] and ca. −50 °C [R = Tol (**20**)] (Scheme 7). However, when monitored by NMR spectroscopy, $Ag[O_2CPh]$ did not react with **19** or **20** at temperatures below those at which **19** and **20** decompose.

Mechanistic Considerations. Diaroyl peroxides react with $PdMe_2(L_2)$ and $PdMeTol(L_2)$ species in a complex series of reactions, affording a combination of carbon−carbon and carbon−oxygen coupling products along with bis(carboxylato)palladium(II) species. The diorganopalladium(II) reagents are expected to undergo an initial oxidative addition to form an undetected "$Pd^{IV}(O_2CAr)_2MeR(L_2)$" (**A**−**C**) intermediate, similar to observations of the reaction of dibenzoyl peroxide with $PtMe_2$(phen) (phen = 1,10-phenanthroline) and $PtAr_2(L_2)$ (Ar = Ph, 4-Tol, 3-Tol, or 4-$MeOC_6H_4$; L_2 = bpy, phen) to form octahedral *cis*,*cis*- and *trans*,*cis*-$Pt^{IV}(O_2CPh)_2Me_2$(phen) and *cis*,*cis*- and *trans*,*cis*-$Pt^{IV}(O_2CPh)_2Ar_2(L_2)$, respectively.[9] The reactions of eq 2, involving oxidative addition of Se−Se bonds to Pd(II), together with more recent observations of reversible oxidative addition of diphenyl diselenide to Pt(4-$MeOC_6H_4$)R(4,4′-Bu^t-6,6′-bpy) [R = $CH(CO_2Me)_2$, $CH(CO_2Et)_2$, $CH(CO_2Pr^i)_2$] to give octahedral $Pt^{IV}(SePh)_2$(4-$MeOC_6H_4$)R(4,4′-Bu^t-6,6′-bpy)[14] and of bis(4-chlorophenyl)diselenide to PdMe(Ar′)(bpy) (Ar′ = 4-Tol, 4-$MeOC_6H_4$) to give octahedral $Pd^{IV}(SeC_6H_4Cl\text{-}4)_2Me(Ar')$(bpy),[15] also provide a model for this reactivity.

The undetected Pd(IV) species are immediately involved in exchange reactions with remaining Pd(II) starting complex to form the detected triorganopalladium(IV) species. Reactions of this type reported to date occur via nucleophilic attack by a Pd(II) reagent at an alkyl group bonded to a Pd(IV) cationic species formed by dissociation of an anionic ligand, to generate a more stable Pd(IV) product and a less nucleophilic Pd(II) product,[11] and thus are consistent with the proposed reactions of eqs 4, 9, and 15 in Schemes 1, 3, and 5. By analogy with reported reactions, including a kinetic study of the reaction of $PdBrMe_2(CH_2Ph)$(phen) with $PtMe_2$(phen),[11a] initial dissociation of one benzoate moiety from "$Pd(O_2CAr)_2MeR(L_2)$" (**A**−**C**) would result in the formation of a five-coordinate intermediate **E** (Scheme 7). As the configurations of **A**−**C** are unknown, isomerization may be required on the pathway to **F**, followed by nucleophilic attack by the diorganopalladium(II) reagent at a methyl group (**F**), with Me^+ transfer forming a new cationic Pd(IV) species (**G**) and the Pd(II) species $Pd(O_2CAr)R(L_2)$ (**5**−**8**, **15**−**18**). Reattachment of the benzoate anion with the newly formed Pd(IV) cation would then lead to the observed, more stable, Pd(IV) species $Pd(O_2CAr)Me_2R(L_2)$ (**1**−**4**, **13**, **14**) and undetected "$Pd(O_2CAr)Me_2Tol$(tmeda)" (**D**).

Decomposition of the triorganopalladium(IV) species (**1**−**4**, **13**, **14**, **D**) by reductive elimination follows, forming a second monoorganopalladium(II) species and carbon−carbon coupling products (eqs 5, 10, 16 in Schemes 1, 3, 5). It is of particular interest that carbon−oxygen coupling does not occur from the *observed* Pd(IV) species, illustrating the complexity of organopalladium(IV) chemistry and the extreme caution needed in deducing mechanisms of catalytic processes on the basis of model reactions.

Synthesis and Characterization of Complexes. Complexes of the form $Pd(O_2CAr)_2(L_2)$ (**9**−**12**), $Pd(O_2CAr)R(L_2)$ (**5**−**8**, **15**, **16**), and $Pd(O_2CAr)Me_2R(L_2)$ (Ar = Ph, Ar_F; L_2 = bpy, tmeda; R = Me, Tol) (**1**−**4**, **13**, **14**) were prepared by metathesis reactions involving $PdCl_2(L_2)$, $PdIR(L_2)$, or $PdIMe_2R(L_2)$ and the appropriate silver(I) salt. On several occasions, significant difficulty was encountered in obtaining pure samples suitable for elemental analysis, although in most instances this was overcome by obtaining the complexes in crystalline form.

(18) Kruis, D.; Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1997**, *532*, 235−242.
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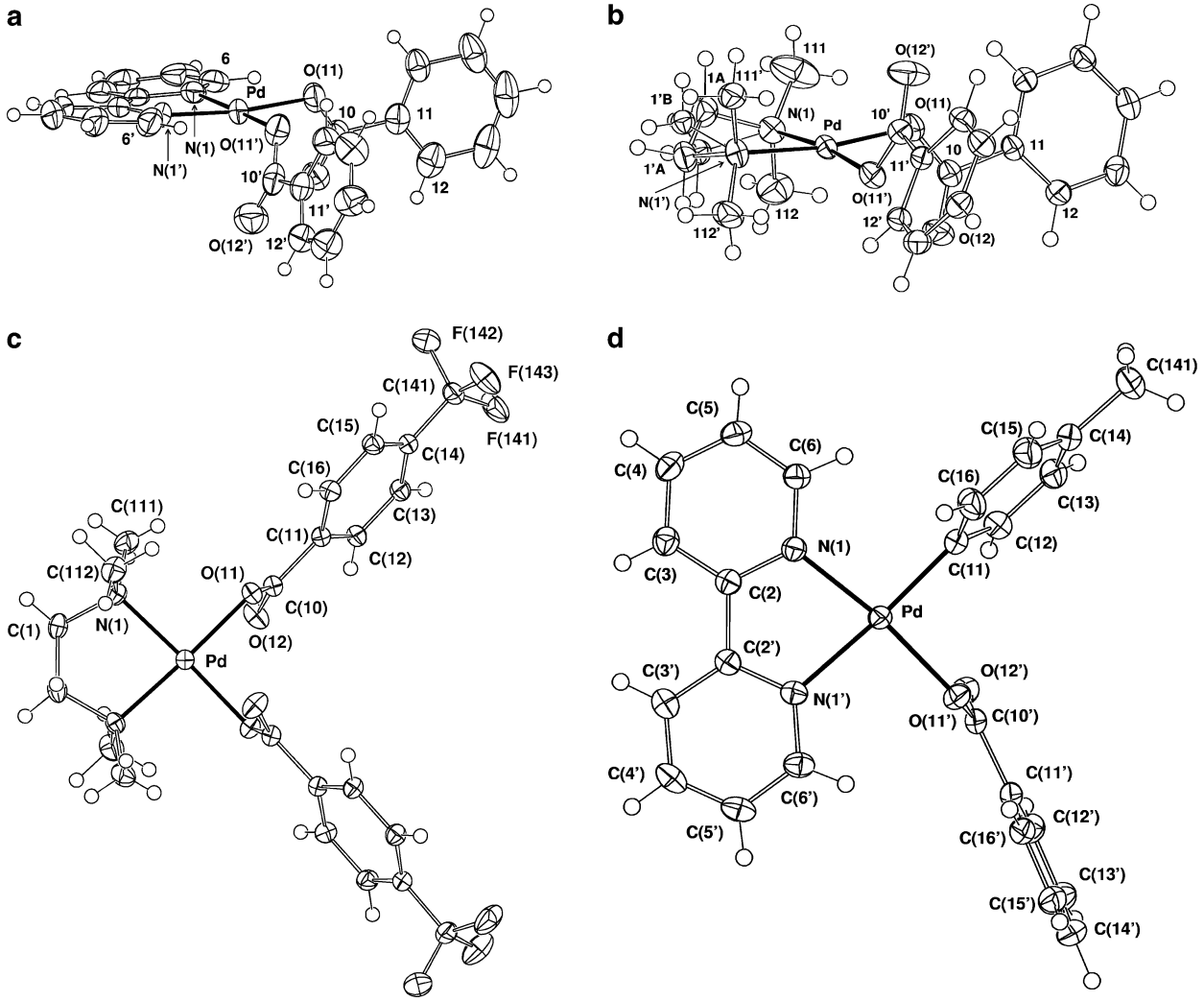

Figure 1. Projections of molecules of (a) $Pd(O_2CPh)_2(bpy)$ (**9**), (b) $Pd(O_2CPh)_2(tmeda)$ (**11**), (c) $Pd(O_2CAr_F)_2(tmeda)$ (**12**), and (d) $Pd(O_2CPh)(Tol)(tmeda)$ (**15**). Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

However, for $Pd(O_2CPh)Me(tmeda)$ (**7**) and $Pd(O_2CPh)$-Tol(bpy) (**15**) several attempts at attaining accurate microanalyses failed. Similar difficulties were experienced by Neo et al. in characterization of a number of palladium(II) phosphine carboxylates.[16]

The unstable Pd(IV) complexes were generated and used in situ and characterized by NMR spectroscopy. ^1H NMR characterization of trimethylpalladium(IV) complexes **1**−**4** was straightforward because of the symmetry of the complexes, the presence of only one isomer, and the consequently uncomplicated spectra. Two isomers were present for the dimethyl(aryl)palladium(IV) complexes (**13**, **14**), the spectra being consistent with the expected facial arrangement of organic ligands. All of the observed Pd(IV) complexes displayed lower stability than the related iodo complexes $PdIMe_3(L_2)$ (L_2 = tmeda, bpy)[17,18] and $PdIMe_2Tol(bpy)$.[11c]

Structural Studies of 9, 11, and 12 and the Dichloromethane Solvate of 15. The complexes are mononuclear, containing approximate square-planar geometry for palladium on the basis of the presence of *cis*-bidentate nitrogen donor ligands (bpy or tmeda) and two unidentate carboxylate groups (**9**, **11**, **12**) or a unidentate carboxylate group and a tolyl group (**15**·CH_2Cl_2) (Figure 1).

In **12**, one-half of the neutral molecule comprises the asymmetric unit of the structure, a crystallographic 2-axis passing through the metal atom and the central bond of the ordered diamine ligand to place the uncoordinated oxygen atoms of carboxylate ligands above and below the mean coordination plane. The other tmeda complex (**11**) has quasi-2 symmetry with the tmeda ligand disordered. The bpy complexes (**9**, **15**·CH_2Cl_2) are devoid of crystallographic symmetry, and a full molecule comprises the asymmetric unit of the structure. In contrast to the tmeda complexes, **9** has the uncoordinated oxygen atoms of the benzoate group to the same side of the coordination plane. In all complexes, the carboxylate CCO_2 planes are quasi-coplanar with their aromatic C_6 parent and lie quasi-normal to the coordination plane. In **12** the Pd−O−C angle is appreciably smaller (∼6−11°) than in the other complexes; the consistency of the other bonding parameters in relation to those across the series suggests that it is unlikely to be a consequence of any electronic effect due to the CF_3 substituent.

Experimental Section

General Procedures. The reagents $PdCl_2(L_2)$,[17] $PdITol(L_2)$,[18] $PdMeTol(L_2)$,[18] $PdIMe_3(L_2)$[11b,19] (L_2 = bpy, tmeda),

PdIMe(tmeda),[17] $PdIMe_2Tol(bpy)$,[18] and $(Ar_FCO_2)_2$[20] were prepared as previously reported; $Ag[O_2CAr_F]$ was prepared as described for the analogue $Ag[O_2CPh]$,[21] and $(PhCO_2)_2$ was used as received (BDH). The complex PdIMe(bpy) was prepared as described for PdIMe(tmeda) but starting with $PdMe_2$(bpy).[17] All other reagents were used as received. NMR spectra were measured on Varian Gemini-200 NMR, Varian INOVA-400 NMR, or Varian Mercury-300 NMR spectrometers. Infrared spectra were measured as KBr disks or Nujol mulls using a Bruker IFS 66 FTIR spectrometer or a Perkin-Elmer Paragon 100 FTIR in the mid-IR range (400−4000 cm^{-1}). Elemental analyses were performed by the Central Science Laboratory, University of Tasmania, using a Carlo Erba EA 1108 elemental analyzer or a ThermoFinnigan Flash EA 1112 elemental analyzer. Coupled GC−MS was carried out using a HP 5890 gas chromatograph fitted with a 25 m × 0.52 mm and connected to a 5970B mass selective detector (70 eV ET with He carrier gas).

Synthesis of Palladium(II) Complexes $Pd(O_2CAr)_2(L_2)$ (Ar = Ph, Ar_F; L_2 = tmeda, bpy) (9−12). General Synthesis. Silver aroate (1.20 mmol) was added to a suspension of $PdCl_2(L_2)$ (0.60 mmol) in dichloromethane (10 mL). The suspension quickly became yellow in color. It was then stirred for 15 min in the absence of light and filtered through a plug of glass fiber filter paper and Celite, and the filtrate was evaporated to dryness in vacuo. The resulting yellow solids were rinsed with *n*-pentane (3 × 5 mL) and dried in vacuo.

$Pd(O_2CPh)_2$(bpy) (9). Yield: 0.23 g (76%). Crystals suitable for the X-ray work were obtained from the reaction of $PdMe_2$(bpy) with $(PhCO_2)_2$ in acetone-d_6 (vide infra). ^1H NMR ($CDCl_3$): δ 8.40 (d, 2H, ^3J = 7.6 Hz, H3), 8.30 (dd, 2H, ^3J = 5.6 Hz, ^4J = 1.0 Hz, H6 bpy), 8.12 (d, 4H, ^3J = 7.2 Hz, ^4J = 1.6 Hz, *ortho*-Ph), 8.08 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.41 (m, 2H, *para*-Ph), 7.34 (m, 4H, *meta*-Ph), 7.26 (ddd [overlaps with solvent peak], 2H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5). IR (KBr disk): $\nu(CO_2)$ 1622 s, 1343 s cm^{-1}. Anal. Calcd: C, 57.10; H, 3.59; N, 5.55. Found: C, 57.05; H, 3.53; N, 5.43.

$Pd(O_2CAr_F)_2$(bpy) (10). Yield: 0.0900 g (93%). ^1H NMR (acetone-d_6): δ 8.70 (d, 2H, ^3J = 7.6 Hz, H3), 8.39 (td, 2H, ^3J = 7.6 Hz, ^4J = 1.6 Hz, H4), 8.32 (dd, 2H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H6), 8.19 (d, 4H, ^3J = 8.0 Hz, *ortho*-Ar_F), 7.73 (ddd, 2H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5), 7.69 (d, 4H, ^3J = 8.0 Hz, *meta*-Ar_F). IR (KBr disk): $\nu(CO_2)$ 1635 s, 1566 m, 1350 s cm^{-1}; $\nu(CF_3)$ 1319 vs cm^{-1}. Anal. Calcd: C, 48.73; H, 2.52; N, 4.37. Found: C, 48.75; H, 2.52; N, 4.19.

$Pd(O_2CPh)_2$(tmeda) (11). Yield: 0.0342 g (96%). Crystals suitable for the X-ray work were obtained from the reaction of $PdMe_2$(tmeda) with $(PhCO_2)_2$ in acetone-d_6 (vide infra). ^1H NMR (acetone-d_6): δ 7.91 (d, 4H, ^3J = 7.6 Hz [complex ^4J coupling also observed], *ortho*-Ph), 7.34 (m, 2H, *para*-Ph), 7.27 (m, 2H, *meta*-Ph), 3.05 (s, 4H, NCH_2), 2.82 (s, 12H, NCH_3). IR (KBr disk): $\nu(CO_2)$ 1616 s, 1576 m, 1336 vs cm^{-1}. Anal. Calcd: C, 51.68; H, 5.64; N, 6.03. Found: C, 51.76; H, 5.61; N, 5.43.

$Pd(O_2CAr_F)_2$(tmeda) (12). Yield: 0.0215 g (38%). Crystals suitable for the X-ray work were obtained from the reaction of $Pd(O_2CAr_F)Me$(tmeda) with $(Ar_FCO_2)_2$ in acetone-d_6 (vide infra). ^1H NMR (CD_2Cl_2): δ 8.04 (d, 4H, ^3J = 7.9 Hz, *ortho*-Ar_F), 7.57 (d, 4H, ^3J = 8.0 Hz, *meta*-Ar_F), 2.85 (s, 4H, NCH_2), 2.79 (s, 12H, NCH_3). ^{13}C NMR (CD_2Cl_2): δ 172.1 (*C*=O), 139.1, 130.6, 125.4, 63.2 (NCH_2), 51.9 (NCH_3). IR (KBr disk): $\nu(CO_2)$ 1622 s, 1564 m, 1356 s cm^{-1}; $\nu(CF_3)$ 1320 vs cm^{-1}. Anal. Calcd: C, 43.98; H, 4.03; N, 4.66. Found: C, 43.90; H, 3.98; N, 4.64.

Synthesis of Palladium(II) Complexes $Pd(O_2CAr)R(L_2)$ (Ar = Ph, Ar_F; R = Me, Tol; L_2 = tmeda, bpy) (5−8, 15−18). General Synthesis. Silver aroate (0.34 mmol) was added to a suspension of $PdIR(L_2)$ (0.31 mmol) in dichloromethane (10 mL). The suspension quickly became yellow in color. It was then stirred for 15 min in the absence of light and filtered through a plug of glass fiber filter paper and Celite, and the filtrate was evaporated to dryness in vacuo. The resulting yellow solids were rinsed with *n*-pentane (3 × 5 mL) and dried in vacuo.

$Pd(O_2CPh)Me(bpy)$ (5). Yield: 0.12 g (97%). ^1H NMR (acetone-d_6): δ 8.60 (d, 1H, ^3J = 5.6 Hz, H6), 8.55 (d, 1H, ^3J = 8.4 Hz, H3′), 8.49 (d, 1H, ^3J = 8.0 Hz, H3), 8.36 (d, 1H, ^3J = 4.8 Hz, H6′), 8.21 (td, 1H, ^3J = 8.0 Hz, ^4J = 1.2 Hz, H4), 8.2−8.0 (m, 3H, *ortho*-Ph and H4′), 7.65 (ddd, 1H, ^3J = 5.6 Hz, ^4J = 1.6 Hz, H5), 7.56 (ddd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5′), 7.5−7.3 (m, 3H, *meta*- and *para*-Ph), 0.87 (s, 3H, PdMe). IR (Nujol mull): $\nu(CO_2)$ 1613 s, 1572 m, 1353 vs cm^{-1}. Anal. Calcd: C, 54.22; H, 4.04; N, 7.02. Found: C, 54.01; H, 3.76; N, 6.81.

$Pd(O_2CAr_F)Me(bpy)$ (6). Yield: 0.081 g (87%). ^1H NMR (acetone-d_6): δ 8.67 (d, 1H, ^3J = 5.6 Hz, H6), 8.57 (d, 1H, ^3J = 8.0 Hz, H3 or H3′), 8.53 (d, 1H, ^3J = 8.0 Hz, H3 or H3′), 8.43 (d, 1H, ^3J = 4.4 Hz, H6′), 8.3−8.2 (m, 3H, *ortho*-Ar_F and H4 or H4′), 8.18 (td, 1H, ^3J = 7.6 Hz, ^4J = 1.6 Hz, H4 or H4′), 7.72 (m, 3H, *meta*-Ar_F and H5 or H5′), 7.64 (dd, 1H, ^3J = 6.4 Hz, ^4J = 1.2 Hz, H5 or H5′), 0.86 (s, 3H, PdMe). IR (Nujol mull): $\nu(CO_2)$ 1626 s, 1563 m, 1352 s; $\nu(CF_3)$ 1321 vs cm^{-1}. Anal. Calcd: C, 48.89; H, 3.24; N, 6.00. Found: C, 48.97; H, 3.29; N, 5.89.

$Pd(O_2CPh)Me$(tmeda) (7). Yield: 0.0222 g (99%). ^1H NMR (acetone-d_6): δ 7.95 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, *ortho*-Ph), 7.4−7.2 (m, 3H, *meta*- and *para*-Ph), 2.84 (m, 2H, NCH_2), 2.69 (s, 6H, NCH_3), 2.62 (m, 2H, NCH_2), 2.50 (s, 6H, NCH_3), 0.28 (s, 3H, PdMe). IR (Nujol mull): $\nu(CO_2)$ 1594 s, 1549 m, ∼1350 vs (overlaps with Nujol peak) cm^{-1}.

$Pd(O_2CAr_F)Me$(tmeda) (8). Yield: 0.0453 g (99%). ^1H NMR (acetone-d_6): δ 8.13 (dd, 2H, ^3J = 8.6 Hz, ^4J = 0.86 Hz, *ortho*-Ar_F), 7.67 (dd, 2H, ^3J = 8.7 Hz, ^4J = 0.68 Hz, *meta*-Ar_F), 2.85 (m, 2H, NCH_2), 2.72 (s, 6H, NCH_3), 2.67 (m, 2H, NCH_2), 2.52 (s, 6H, NCH_3), 0.32 (s, 3H, PdMe). IR (Nujol mull): $\nu(CO_2)$ 1621 s, 1574 m, 1360 s; $\nu(CF_3)$ 1320 vs cm^{-1}. Anal. Calcd: C, 42.21; H, 5.43; N, 6.56. Found: C, 42.09; H, 5.56; N, 6.45.

$Pd(O_2CPh)Tol$(bpy) (15). Yield: 0.0209 g (100%). Crystals suitable for the X-ray work were obtained from the slow diffusion of *n*-pentane into a CH_2Cl_2 solution of **15**. ^1H NMR (acetone-d_6): δ 8.58 (m, 2H, H3 and H3′), 8.45 (dd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H6′), 8.26 (m, 3H, H6, H4 and H4′), 8.02 (m, 2H, *ortho*-Ph), 7.70 (ddd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5′), 7.59 (ddd, 1H, ^3J = 6.0 Hz, ^4J = 1.2 Hz, H5), 7.41 (d, 2H, ^3J = 8.0 Hz, *ortho*-Tol) 7.40−7.28 (m, 3H, *meta*- and *para*-Ph and *ortho*-Tol), 6.79 (dd, 2H, ^3J = 8.0 Hz, ^4J = 0.6 Hz, *meta*-Tol), 2.20 (s, 3H, Me). IR (Nujol mull): $\nu(CO_2)$ 1598 s, 1571 m, 1347 vs cm^{-1}.

$Pd(O_2CAr_F)Tol$(bpy) (16). Yield: 0.0286 g (100%). ^1H NMR (acetone-d_6): δ 8.58 (d, 2H, ^3J = 8.0 Hz, H3 and H3′), 8.44 (d, 1H, ^3J = 4.8 Hz, H6′), 8.25 (m, 3H, H6, H4 and H4′), 8.18 (d, 2H, ^3J = 8.0 Hz, *ortho*-Ar_F), 7.7 (m, 3H, H5′ and *meta*-Ar_F), 7.58 (t, 1H, ^3J = 5.2 Hz, H5), 7.39 (d, 2H, ^3J = 8.0 Hz, *ortho*-Tol), 6.80 (d, 2H, ^3J = 7.8 Hz, *meta*-Tol), 2.21 (s, 3H, Me). IR (Nujol mull): $\nu(CO_2)$ 1627 s, 1573 m, ∼1360 m (overlaps with Nujol peak) cm^{-1}; $\nu(CF_3)$ 1320 vs cm^{-1}. Anal. Calcd: C, 55.31; H, 3.53; N, 5.16. Found: C, 55.03; H, 3.48; N, 5.01.

$Pd(O_2CPh)Tol$(tmeda) (17). Yield: 0.039 g (99%). ^1H NMR (acetone-d_6): δ 7.86 (dd, 2H, ^3J = 8.4 Hz, ^4J = 1.6 Hz, *ortho*-Ph), 7.34 (d, 2H, ^3J = 8.0 Hz, *ortho*-Tol), 7.3−7.2 (m, 3H, *meta*- and *para*-Ph), 6.64 (dd, 2H, ^3J = 8.0 Hz, ^4J = 0.6 Hz, *meta*-Tol), 2.91 (m, 2H, NCH_2), 2.17 (m, 2H, NCH_2), 2.55 (s, 6H, NCH_3), 2.53 (s, 6H, NCH_3), 2.10 (s, 3H, Me). IR (Nujol mull): $\nu(CO_2)$ 1614 s, 1574 m, 1352 vs cm^{-1}. Anal. Calcd: C, 55.24; H, 6.49; N, 6.44. Found: C, 55.36; H, 6.29; N, 6.53.

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Preparation of Pd(O_2CAr_F)Tol(tmeda) (18). Yield: 0.022 g (92%). ^{1}H NMR (acetone-d_6): δ 8.01 (dd, 2H, ^3J = 8.2 Hz, ^4J = 0.8 Hz, *ortho*-Ar_F), 7.57 (dd, 2H, ^3J = 8.2 Hz, ^4J = 0.8 Hz, *meta*-Ar_F), 7.32 (d, 2H, *ortho*-Tol), 6.64 (d, 2H, ^3J = 7.6 Hz, *meta*-Tol), 2.95 (m, 2H, NCH_2), 2.74 (m, 2H, NCH_2), 2.58 (s, 6H, NCH_3), 2.56 (s, 6H, NCH_3), 2.12 (s, 3H, Me). IR (Nujol mull): ν(CO_2) 1613 s, 1572 m, ~1360 s (overlaps with Nujol peak); ν(CF_3) 1321 vs. Anal. Calcd: C, 50.16; H, 5.41; N, 5.57. Found: C, 50.30; H, 5.33; N, 5.56.

In Situ Synthesis of Palladium(IV) Complexes Pd(O_2CAr)Me_2R(L_2) (Ar = Ph, Ar_F; R = Me, Tol; L_2 = tmeda, bpy) (1−4, 13, 14). General Synthesis. Iodomethane (1 mL) was cooled to −35 °C. To this was added PdMeR(L_2) (0.0294 mmol) and the solution stirred for 30 min. The volatile components were removed in vacuo at low temperature, leaving a pale yellow solid, [PdIMe_2R(L_2)]. The solid was redissolved in acetone-d_6 (0.6 mL) at −70 °C. To this was added silver aroate (0.0297 mmol), and a reaction was observed immediately. The suspension was stirred for 30 min at −50 °C, then quickly filtered through a plug of glass fiber filter paper into a precooled NMR tube.

***fac*-Pd(O_2CPh)Me_3(bpy) (1).** ^{1}H NMR (acetone-d_6, −30 °C): δ 9.01 (d, 2H, ^3J = 4.0 Hz, H6), 8.59 (d, 2H, ^3J = 8.0 Hz, H3), 8.22 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.79 (ddd, 2H, ^3J = 5.2 Hz, ^4J = 1.2 Hz, H5), 7.65 (d, 2H, ^3J = 6.4 Hz, *ortho*-Ph), 7.18 (t, 1H, ^3J = 6.8 Hz, *para*-Ph), 7.11 (t, 2H, ^3J = 7.2 Hz, *meta*-Ph), 1.72 (s, 6H, PdMe), 0.64 (s, 3H, PdMe).

***fac*-Pd(O_2CAr_F)Me_3(bpy) (2).** ^{1}H NMR (acetone-d_6, −30 °C): δ 9.03 (dd, 2H, ^3J = 5.6 Hz, ^4J = 0.8 Hz, H6), 8.40 (d, 2H, ^3J = 8.0 Hz, H3), 8.26 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.84−7.51 (m, 4H, H5 and *ortho*-Ar_F), 7.50 (d, 2H, ^3J = 8.0 Hz, *meta*-Ar_F), 1.71 (s, 6H, PdMe), 0.69 (s, 3H, PdMe).

***fac*-Pd(O_2CPh)Me_3(tmeda) (3).** ^{1}H NMR (acetone-d_6, −40 °C): δ 7.99 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, *ortho*-Ph), 7.35 (m, 3H, *meta*- and *para*-Ph), 3.0 (br, 2H, NCH_2), 2.7 (br, 2H, NCH_2), 2.49 (s, 6H, NCH_3), 2.36 (s, 6H, NCH_3), 1.53 (s, 6H, PdMe), 0.78 (s, 3H, PdMe).

***fac*-Pd(O_2CAr_F)Me_3(tmeda) (4).** ^{1}H NMR (acetone-d_6, −40 °C): δ 8.18 (d, 2H, ^3J = 8.4 Hz, *ortho*-Ar_F), 7.72 (d, 2H, ^3J = 8.4 Hz, *meta*-Ar_F), 3.20−2.82 (br, 2H, NCH_2), 2.82−2.60 (br, 2H, NCH_2), 2.50 (s, 6H, NCH_3), 2.37 (s, 6H, NCH_3), 1.53 (s, 6H, PdMe), 0.82 (s, 3H, PdMe).

Pd(O_2CPh)Me_2Tol(bpy) (13). 13a: ^{1}H NMR δ 9.36 (dd, 2H, ^3J = 4.8 Hz, ^4J = 0.8 Hz, H6), 8.42 (d, 2H, ^3J = 8.4 Hz, H3), 8.15 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.84 (ddd, 2H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5), 7.68 (m [overlaps with other isomer], *ortho*-Ph), 7.19 (m [overlaps with other isomer], *para*-Ph), 7.14 (m [overlaps with other isomer], *meta*-Ph), 6.87 (d, 2H, ^3J = 8.0 Hz, *ortho*-Tol), 6.61 (d, 2H, ^3J = 7.6 Hz, *meta*-Tol), 2.09 (s, 6H, PdMe), 2.08 (s, 3H, Me). **13b**: δ 9.08 (d, 1H, ^3J = 5.6 Hz, H6), 8.60 (m, 2H, H3 and H3′), 8.52 (dd, 1H, ^3J = 5.2 Hz, ^4J = 1.2 Hz, H6′), 8.20 (m, 2H, H4 and H4′), 7.79 (ddd, 1H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5), 7.68 (m [overlaps with other isomer], *ortho*-Ph, H5′), 7.19 (m [overlaps with other isomer], *para*-Ph), 7.14 (m [overlaps with other isomer], *meta*-Ph), 7.03 (d (br), 2H, ^3J = 8.0, *meta*-Tol), 2.29 (s, 3H, Me), 2.00 (s, 3H, PdMe), 1.14 (s, 3H, PdMe).

Pd(O_2CAr_F)Me_2Tol(bpy) (14). ^{1}H NMR (acetone-d_6, −30 °C): **14a**: δ 9.34 (d, 2H, ^3J = 5.2 Hz, H6), 8.49 (d, 2H, ^3J = 8.4 Hz, H3), 8.20 (td, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H4), 7.86 (ddd, 2H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H5) 7.83 (m [overlaps with other isomer], *ortho*-Ar_F), 7.50 (d [overlaps with other isomer], ^3J = 8.0 Hz, *meta*-Ar_F), 6.88 (d, 2H, ^3J = 8.0 Hz, *ortho*-Tol), 6.63 (d, 2H, ^3J = 8.0 Hz, *meta*-Tol), 2.11 (s, 6H, PdMe), 2.08 (s, 3H, Me); **14b**: δ 9.08 (dd, 1H, ^3J = 5.2 Hz, ^4J = 0.8 Hz, H6), 8.64 (d, 2H, ^3J = 8.0 Hz, H3 and H3′), 8.52 (dd, 1H, ^3J = 5.2 Hz, ^3J = 0.8 Hz, H6′), 8.24 (m, 2H, H4 and H4′), 7.83 (m [overlaps with other isomer], *ortho*-Ar_F, H5), 7.71 (ddd, 1H, ^3J = 5.6 Hz, ^4J = 1.2 Hz, H5′), 7.50 (d [overlaps with other isomer], ^3J = 8.0 Hz, *meta*-Ar_F), 7.04 (d (br), 2H, ^3J = 7.6 Hz, *meta*-Tol), 2.29 (s, 3H, Me), 2.02 (s, 3H, PdMe), 1.20 (s, 3H, PdMe).

^{1}H NMR Studies of the Reaction of Palladium(II) Complexes with ($ArCO_2$)$_2$ (Ar = Ph, Ar_F). PdMeR(L_2) (R = Me, Tol; L = bpy, tmeda) with ($ArCO_2$)$_2$. In a typical experiment, a solution of PdMeR(L_2) in acetone-d_6 (0.3 mL) in an NMR tube was cooled to ≤ThinSpace−50 °C. To this was added a solution of ($ArCO_2$)$_2$ in acetone-d_6 (0.3 mL) in the ratios outlined in the Results section. The tube was placed in a NMR probe, precooled to ≤ThinSpace−50 °C, and the solution was warmed in 10 °C intervals with monitoring. Products of the reaction were identified by GC−MS and by comparison of the observed ^{1}H NMR to the ^{1}H NMR of known and independently synthesized compounds.

Pd(O_2CAr)R(L_2) (R = Me, Tol; L = bpy, tmeda) with ($ArCO_2$)$_2$. In a typical experiment, a solution of ($ArCO_2$)$_2$ in acetone-d_6 (0.3 mL) was added to a solution of Pd(O_2CAr)R(L_2) in acetone-d_6 (0.3 mL) and allowed to go to completion at ambient temperature (several hours for R = Me and several days for R = Tol). Products of the reaction were identified by GC−MS and by comparison of the observed ^{1}H NMR to the ^{1}H NMR of known and independently synthesized compounds.

^{1}H NMR Studies of the Reaction of Diiodine with PdMeR(bpy) (R = Me, Tol). In a typical experiment, a solution of I_2 in acetone-d_6 (0.4 mL) in an NMR tube was cooled to ~ThinSpace−50 °C. To this was added a solution of PdMeR(bpy) in acetone-d_6 (0.3 mL) in 1:1 ratio. ^{1}H NMR spectra showed the presence of PdI_2MeR(bpy) (**19**, **20**) (see below). The solutions were warmed in 10 °C intervals with monitoring. Iodomethane and PdIMeR(bpy) were formed at ca. ThinSpace−10 °C (R = Me) and at −50 °C (R = Tol).

PdI_2Me_2(bpy) (19). ^{1}H NMR (acetone-d_6, −40 °C): δ 9.01 (d, 2H, ^3J = 5.6 Hz, H6), 8.77 (d, 2H, ^3J = 8.4 Hz, H3), 8.32 (t, 2H, ^3J = 7.6 Hz, H4), 7.86 (t, 2H, ^3J = 6.8 Hz, H5), 2.75 (s, 6H, PdMe).

PdI_2MeTol(bpy) (20). ^{1}H NMR (acetone-d_6, −50 °C): δ 9.12 (d, 1H, ^3J = 4.8 Hz, H6 or H6′), 8.94 (d, 1H, ^3J = 4.4 Hz, H6 or H6′), 8.85 (m, 2H, H3 and H3′), 8.35 (m, 2H, H4 and H4′), 7.99 (d, 2H, ^3J = 8.4 Hz, *ortho*-Tol), 7.88 (m, 2H, H5 and H5′), 6.90 (d, 2H, ^3J = 8.4 Hz, *meta*-Tol), 3.19 (s, 3H, Me), 2.30 (s, 3H, PdMe).

X-ray Data Collection, Structure Determination, and Refinement for 9, 11, and 12 and the Solvated Crystal Containing Molecules of 15. Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation, λ = 0.7107$_3$ Å; *T* ca. 153 K), yielding $N_{t(otal)}$ reflections, these merging to *N* unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed" and used in the full matrix least-squares refinements. Anisotropic displacement parameter forms were refined, (x,y,z,U_{iso})$_H$, also. Conventional residuals *R*, R_w (weights: $((\sigma^2(F) + 0.0004F^2)^{-1})$ on $|F|$ are quoted at convergence. Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[22] Figure 1 depicts non-hydrogen atoms with 50% probability amplitude displacement envelopes, hydrogen atoms where shown having arbitrary radii of 0.1 Å.

Variata. Complex **9**: (x,y,z,U_{iso})$_H$ were constrained at estimates in the refinement. Complex **11**: Disorder was modeled in the hydrocarbon bridge of the chelate in terms of pairs of methylene sites, occupancies 0.770(5), and complement, not being resolvable beyond. (x,y,z,U_{iso})$_H$ were constrained throughout in the refinement at estimates. Complex **15**: The dichloromethane solvent molecule was modeled in terms of two components with common carbon, occupancies

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refining to 0.778(2) and complement; $(x,y,z,U_{iso})_H$ (solvent only) were not refined.

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Supporting Information Available: Atomic parameters, bond distances and angles, and crystallographic details for **9**, **11**, **12**, and **15**·CH_2Cl_2, and ^{1}H NMR spectra of representative reaction sequences. This material is available free of charge via the Internet at http://pubs.acs.org.

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