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Direct Arylation of 2-Methylthiophene with Isolated [PdAr(μ-O_2CR)(PPh_3)]$_n$ Complexes: Kinetics and Mechanism

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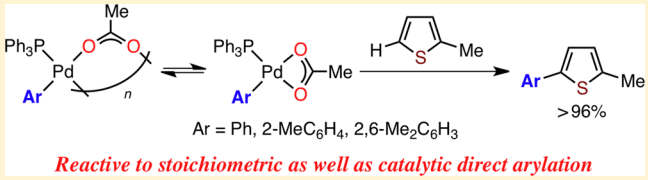
Supporting Information

ABSTRACT: The palladium-catalyzed direct arylation of aromatic compounds with aryl halides has been proposed to involve an arylpalladium carboxylate intermediate. However, isolated arylpalladium complexes, which undergo C−H bond cleavage of aromatic substrates without the aid of additional activators or promoters, have been scarcely documented. This paper reports that [PdAr(μ-O_2CR)(PPh_3)]$_n$ complexes (**1**: Ar = Ph, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$; R = Me, ^{t}Bu) successfully react with 2-methylthiophene (**2**) in the absence of additives to afford 5-aryl-2-methylthiophenes (**3**) in high yields. The reactivity increases with increasing bulkiness of the Ar group, whereas the bulky pivalate ligand (R = ^{t}Bu) reduces the reactivity as compared with the acetate ligand (R = Me). Complex **1** is in equilibrium with the monomeric species [PdAr(O_2CR-κ^2O)(PPh_3)] (**5**) in solution, as confirmed by IR spectroscopy. Kinetic examinations have suggested that the direct arylation proceeds via **5**, which undergoes C−H bond cleavage of **2**. Complex **1** serves as a good catalyst for direct arylation of **2** with aryl bromides.

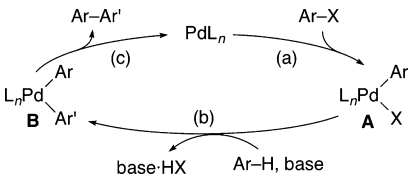


INTRODUCTION

Dehydrohalogenative coupling of aromatic compounds with aryl halides catalyzed by palladium complexes (so-called direct arylation) has attracted a great deal of attention.[1] It has been recognized that direct arylation is advantageous over traditional cross-coupling reactions in terms of reduced waste generation and fewer reaction steps. Moreover, direct arylation that does not need organometallic reagents has excellent functional group tolerance. In this context, a number of studies have been carried out to improve the catalytic activity and to expand the substrate scope.[2] Recently, direct arylation has been applied to polycondensation reactions giving π-conjugated polymers.[3]

Scheme 1 outlines a generally accepted catalytic cycle for Pd(0)-catalyzed direct arylation, which is basically similar to that for cross-coupling reactions.[1] A distinct difference between the two catalytic cycles exists in the conversion of monoarylpalladium **A** into diarylpalladium **B** (step b). Cross-coupling involves the transmetalation of **A** with organometallic reagents, whereas direct arylation requires C−H bond cleavage of aromatic substrates on **A**, and this step is often assumed as the turnover limit in the catalytic cycle.[2f]

Scheme 1. Plausible Catalytic Cycle for Direct Arylation



Recent theoretical studies have suggested the intermediacy of an arylpalladium carboxylate, which undergoes C−H bond cleavage of aromatic substrates, typically via a concerted metalation−deprotonation (CMD) pathway.[4,5] However, isolated aryl complexes that undergo C−H bond cleavage of aromatic compounds have been extremely limited.[6−9] Mori and co-workers reported that [PdAr(X)(bipy)] (X = I, Br, Cl) reacted with thiophenes to afford the corresponding arylthiophenes in good to high yields, where the addition of $AgNO_3$ and KF to the system was essential for the reaction to proceed.[6] More recently, Hartwig and co-workers carried out detailed kinetic examinations using [PdAr(O_2CMe-κ^2O)(P^tBu_3)].[8] They found that the arylpalladium acetate itself is poorly reactive, but it coupled with pyridine *N*-oxide via a cooperative C−H functionalization process with the aid of a cyclometalated complex.[8b] Thus, although theoretical studies have suggested a simple reaction process for the conversion of **A** to **B**, isolated arylpalladium complexes, which are reactive to aromatic compounds without the aid of additional activators or promoters, have been scarcely documented.

Herein, we disclose that arylpalladium complexes of the formula [PdAr(μ-O_2CR)(PPh_3)]$_n$ (**1**, eq 1) react with 2-methylthiophene (**2**) to afford 5-aryl-2-methylthiophenes (**3**) as direct arylation products in high yields. The reactions successfully proceed without the use of additives. Kinetic and structural examinations have suggested that **1** is interconverted with the monomeric species [PdAr(O_2CR-κ^2O)(PPh_3)] (**5**) in solution, and **5** reacts with **2** to afford **3**.

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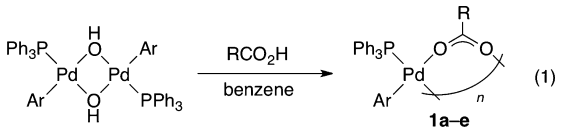


(1)

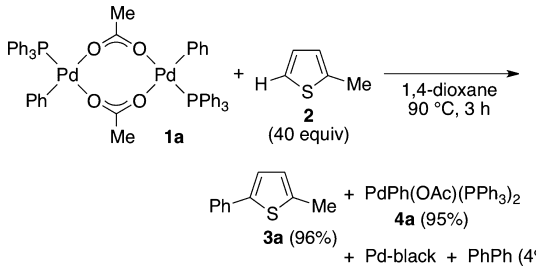
Ar	R	n	
Ph	Me	2	**1a**
2-MeC$_6$H$_4$	Me	2	**1b**
2,6-Me$_2$C$_6$H$_3$	Me	4	**1c**
Ph	^{t}Bu	2	**1d**
Ph	CF$_3$	2	**1e**

RESULTS AND DISCUSSION

Synthesis and Reactions of 1. Complexes **1a**–**e** having three kinds of aryl and carboxylate ligands were prepared by the treatment of the corresponding μ-hydroxy complexes with carboxylic acids, according to the synthetic procedure for **1a** (eq 1).[10] X-ray diffraction analysis revealed that 2-methylphenyl (**1b**) and phenyl (**1d**) complexes adopt a dimeric structure with μ-carboxylate ligands, similarly to **1a**,[11] whereas 2,6-dimethylphenyl complex **1c** is a tetramer of the [Pd(2,6-Me$_2$C$_6$H$_3$)(μ-O$_2$CMe)(PPh$_3$)] units in the crystal (vide infra).

Treatment of **1a** (10 μmol, 18 mM) with 2-methylthiophene (**2**, 0.40 mmol, 40 equiv/**1a**) in 1,4-dioxane at 90 °C for 3 h afforded 5-phenyl-2-methylthiophene (**3a**, 9.6 μmol, 96%/**1a**) and [PdPh(O$_2$CMe)(PPh$_3$)$_2$] (**4a**), along with deposition of Pd-black and a small amount of biphenyl (0.4 μmol, 4%/**1a**) (Scheme 2). The formation of **3a** and biphenyl was confirmed

Scheme 2. Reaction of 1a with 2-Methylthiophene (2)



by HPLC using C$_6$Me$_6$ as an internal standard. The reaction solution was evaporated, dissolved in CD$_2$Cl$_2$, and examined by NMR spectroscopy, showing the absence of **1a** and the formation of **4a** (9.5 μmol, 95%/**1a**). These observations indicate that one-half of **1a** is converted to **2** and Pd-black, and the other half is converted to **4a**, while the biphenyl formation takes place in a small quantity as well.

The reaction was particularly smooth in dimethylacetamide (DMA) as a polar solvent.[12] The bis-PPh$_3$ complex **4a** was clearly less reactive than the mono-PPh$_3$ complex **1a**.[13] Moreover, the iodide [PdPh(μ-I)(PPh$_3$)]$_2$ and hydroxy [PdPh(μ-OH)(PPh$_3$)]$_2$ complexes did not react with **2**.

Kinetic Studies. Figure 1 shows the time course of the formation of **3a** and biphenyl in the reaction of **1a** with **2** (40 equiv) in 1,4-dioxane at 90 °C. Both compounds were simultaneously produced in the system. Their formation continued at a slower rate after the total yield reached 100%/**1a**, due to the slow conversion of **4a**.[13] As a result, the first-order plot gradually deviated from a straight line (Figure 2a), but the formation rate of **3a** could be estimated from the early stage of the plot. The rate constants observed at five different concentrations of **2** exhibited a good linear correlation with the [**2**]$_0$ values (Figure 2b). The kinetic data were consistent with

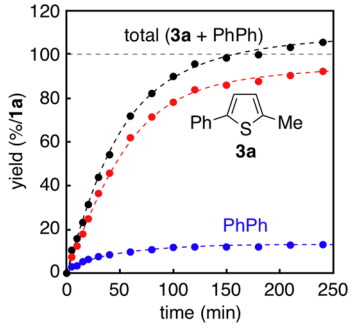


Figure 1. Time course of the formation of **3a** and PhPh in the reaction of **1a** (18 mM) with **2** (0.72 M) in 1,4-dioxane at 90 °C, followed by HPLC using C$_6$Me$_6$ as an internal standard.

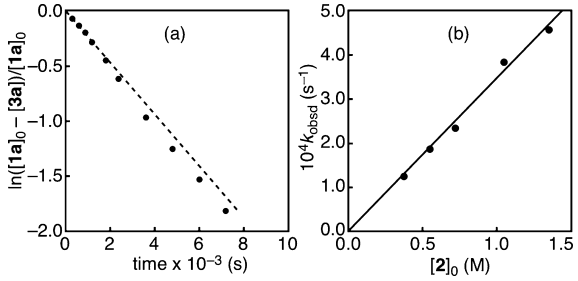


Figure 2. (a) First-order plot for the formation of **3a** in the reaction of **1a** (18 mM) with **2** (0.72 M) in 1,4-dioxane at 90 °C. (b) Plot of first-order rate constants (k_{obsd}) against the concentrations of **2** in 1,4-dioxane at 90 °C.

the following rate equation: d[**3a**]/dt = k_2[**1a**][**2**] (k_2 = 3.5(2) × 10^{-4} s^{-1} M^{-1}).

In the above experiments, we noticed that the amounts of biphenyl varied with experimental procedures. The reaction in Scheme 2 was examined in a gastight NMR sample tube, degassed through freeze–pump–thaw cycles, where 4%/**1a** of biphenyl was formed. On the other hand, the kinetic runs given in Figures 1 and 2 were carried out using standard Schlenk techniques under a nitrogen atmosphere to perform repeated sampling for HPLC analysis, where 12–16%/**1a** of biphenyl was formed. Since the contamination with air could be a reason for the increasing amounts of biphenyl, further experiments were conducted in a gastight NMR sample tube. In this case, the reaction progress was followed by NMR spectroscopy, and organic products were analyzed by HPLC at 100% conversion of the starting complex **1**.

Table 1 summarizes the effects of acetic acid (AcOH), pivalic acid (PivOH), and ^{i}Pr$_2$NEt on the reaction of **1a** with **2**. The

Table 1. Effects of Carboxylic Acids and ^{i}Pr$_2$NEt on the Reaction of 1a with 2 in 1,4-Dioxane at 90 °C[a]

entry	additive (mM)	$t_{1/2}$ (min)[b]	product ratio **3a**:PhPh
1	none	46	96:4
2	AcOH (20)	66	83:17
3	AcOH (39)	139	81:19
4	PivOH (20)	131	95:5
5	PivOH (39)	231	95:5
6	^{i}Pr$_2$NEt (20)	53	98:2
7	^{i}Pr$_2$NEt (39)	56	98:2

[a]Reaction conditions: [**1a**]$_0$ = 18 mM, [**2**]$_0$ = 0.72 M. [b]Half-lives of **1a** estimated by ^{31}P{^{1}H} NMR spectroscopy.

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addition of AcOH and PivOH caused a notable drop in the reactivity (entries 1–5). On the other hand, the effect of $^{i}Pr_2NEt$ was relatively small, while the selectivity for **3a** was slightly improved (entries 6, 7).

Table 2 compares the reactions of **1a–e** with **2** in THF at 65 °C. Interestingly, the reactivity of acetate complexes **1a–c**

Table 2. Effects of Ar and RCO_2 Ligands on the Reactions of 1a–e with 2 in THF at 65 °C[a]

entry	Ar	R		$t_{1/2}$ (min)[b]	product ratio 3:ArAr
1	Ph	Me	(**1a**)	176	91:9
2	2-MeC_6H_4	Me	(**1b**)	89	100:0
3	2,6-$Me_2C_6H_3$	Me	(**1c**)	57	100:0
4	Ph	^{t}Bu	(**1d**)	559	93:7
5	Ph	CF_3	(**1e**)	550	45:55

[a]Reaction conditions: $[\mathbf{1}]_0$ = 18 mM except for **1c** (9 mM), $[\mathbf{2}]_0$ = 0.72 M. [b]Half-lives of **1** estimated by $^{31}P\{^{1}H\}$ NMR spectroscopy.

increased with increasing bulkiness of Ar groups: **1a** < **1b** < **1c** (entries 1–3). Since the selectivity for direct arylation products **3** (5-aryl-2-methylthiophenes) was also improved, it was considered that a bulky Ar group enhanced the reactivity toward **2**. Pivalate (**1d**) and trifluoroacetate (**1e**) complexes were clearly less reactive than the acetate complexes, and **1e** formed biphenyl as the major product (entries 4, 5).

Structural Examinations. The reactivity difference between **1a–d** was correlated with their solution structures. Figure 3 shows the IR spectra of **1c** in a solid (KBr) and a

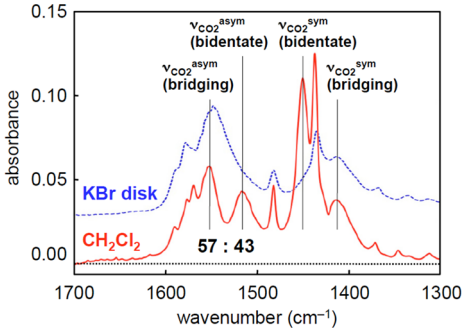

Figure 3. IR spectra of **1c** in KBr and CH_2Cl_2 ([Pd] = 20 mM).

solution (CH_2Cl_2). This complex has a tetrameric form of the [Pd(2,6-$Me_2C_6H_3$)(μ-O_2CMe)(PPh_3)] units in the solid state (Figure S2), showing the ν_{CO2}^{asym} and ν_{CO2}^{sym} bands at 1548 and 1413 cm^{-1}, respectively. The difference between the two absorptions ($\Delta\nu_{CO2}$ = 135 cm^{-1}) is consistent with the bridging coordination of acetate ligands.[14]

On the other hand, **1c** dissolved in CH_2Cl_2 ($[\mathbf{1c}]_0$ = 5 mM; [Pd] = 20 mM) exhibited two sets of ν_{CO2} bands. The absorptions at 1551 and 1413 cm^{-1} are due to the tetrameric complex **1c** with bridging acetates, whereas those observed at 1516 and 1450 cm^{-1} ($\Delta\nu_{CO2}$ = 66 cm^{-1}) are assignable to the monomeric complex [Pd(2,6-$Me_2C_6H_3$)(O_2CMe-κ^2O)(PPh_3)] (**5c**), having a bidentate acetate ligand.[15] Since the $^{31}P\{^{1}H\}$ NMR spectrum was significantly broadened at room temperature, it was concluded that the tetrameric and monomeric complexes are rapidly interconverted with each other in solution (eq 2).

The structures of **1a**, **1b**, and **1d** were similarly examined by IR spectroscopy. Table 3 summarizes the results, together with

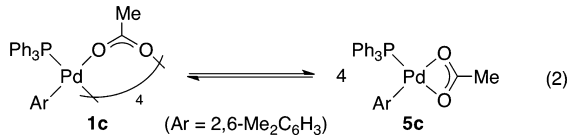

Table 3. IR Data for 1a–d in KBr and CH_2Cl_2 (cm^{-1})

		solution (CH_2Cl_2)[a]		
complex	solid (KBr)[a]	bridging (**1**)	bidentate (**5**)	ratio[b] **1**:**5**
1a	1578, 1415	1578, 1419	–[c]	100:0
1b	1581, 1417	1581, 1416	1517, 1450	84:16
1c	1548, 1413	1551, 1413	1516, 1450	57:43
1d	1577, 1415	1577, 1415	–[c]	100:0

[a]Wavenumbers of ν_{CO2}^{asym} and ν_{CO2}^{sym} absorptions in KBr or CH_2Cl_2 ([Pd] = 20 mM). [b]Ratio of the ν_{CO2}^{asym} absorptions of bridging (**1**) and bidentate (**5**) complexes. [c]Not observed.

the data for **1c**. Unlike **1c**, complexes **1a**, **1b**, and **1d** adopt dimeric structures bridged by two μ-acetate ligands in the solid state, showing the ν_{CO2}^{asym} and ν_{CO2}^{sym} bands at around 1580 and 1415 cm^{-1}, respectively ($\Delta\nu_{CO2} \approx 165$ cm^{-1}). In CH_2Cl_2, **1b** exhibited small absorptions arising from the monomeric species [Pd(2-MeC_6H_4)(O_2CMe-κ^2O)(PPh_3)] (**5b**) (1517 and 1450 cm^{-1}; $\Delta\nu_{CO2}$ = 67 cm^{-1}), in addition to the absorptions of the parent dimer **1b**. In contrast, **1a** and **1d** showed no notable absorptions assignable to monomeric species. With consideration of the absorbance values of ν_{CO2}^{asym} bands, it was concluded that the amount of monomeric species generated from the parent dimer or tetramer in solution increases in the order **1d** ≈ **1a** < **1b** < **1c**. This order is in accordance with the increasing reactivity order of these complexes toward 2-methylthiophene (**2**).

Figure 4 shows the crystal structure of μ-pivalate complex **1d**, which adopts a folded structure of two square-planar units, connected by two μ-pivalate ligands. The phenyl ligand on one of the square-planar units is located close to the PPh_3 ligand on the other square-planar unit, and they undergo steric repulsion from each other. On the other hand, the ^{t}Bu groups of pivalate

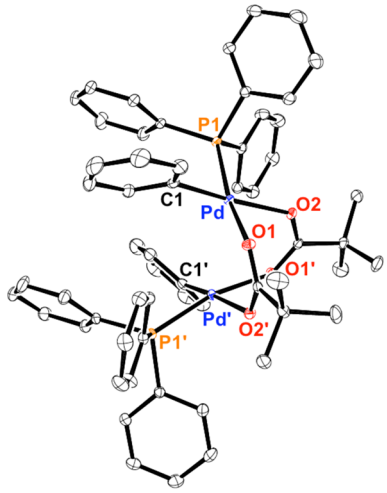

Figure 4. Crystal structure of **1d**·CH_2Cl_2 with 30% probability ellipsoids. Hydrogen atoms and a CH_2Cl_2 molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd–C1 = 1.987(3), Pd–P1 = 2.2368(7), Pd–O1 = 2.111(2), Pd–O2 = 2.118(2), C1–Pd–P1 = 89.83(8), O1–Pd–O2 = 88.22(8).

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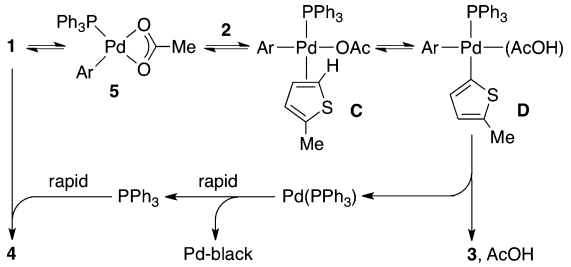
ligands are extruded outside the molecule and, thus, are much less sterically demanding for the molecular structure. Dimeric complexes **1a**[11] and **1b** (Figure S1) displayed similar crystal structures.

Reflecting these structural features, the folding angle between two coordination planes was almost the same for μ-acetate (**1a**, 49.1°) and μ-pivalate (**1d**, 48.9°) complexes (Table S1). In contrast, the folding angle of **1b**, having a bulky 2-methylphenyl ligand (57.4°), was clearly wider than that of phenyl complexes (49.0 ± 0.1°). Thus, it is likely that the dimeric form of **1b** is unstable for steric reasons and prone to dissociate to the monomeric form **5b** in solution. Although the steric condition of tetrameric **1c** could not be simply compared with that of the dimeric analogues, it seems reasonable that the bulky 2,6-dimethylphenyl ligand in **1c** leads to a marked propensity to form the monomeric complex **5c** in solution.

Reaction Mechanism. Accordingly, the formation process of **3** from **1** and **2** would be described as shown in Scheme 3.

Scheme 3. Proposed Mechanism for Reaction of 1 and 2



Although complex **1** exists as a dimer or tetramer of the [PdAr(μ-O_2CR)(PPh_3)] units in the solid state, they are in equilibrium with the monomeric complex **5** in solution. Since the reactivity of **1** is clearly enhanced by increasing the amount of **5**, it is reasonable that product **3** is formed from **5**. Coordination of **2** to **5**, followed by C−H bond cleavage of the thiophene ligand on **C**, forms an aryl−thienyl intermediate **D**, which reductively eliminates **3**, along with the formation of [Pd(PPh_3)] and AcOH. Probably, the highly coordinatively unsaturated Pd(0) species thus generated rapidly decomposes under the reaction conditions to provide free PPh_3 and Pd-black. The free PPh_3 then combines with a part of **1** to form [PdAr(O_2CR)(PPh_3)$_2$] (**4**).

Catalytic Properties of 1. Complex **1a** served as a good catalyst for direct arylation of 2-methylthiophene (**2**) with aryl bromides. Figure 5 demonstrates the competitive formation of **3a** and **3c** in the catalytic reaction of **2** with PhBr and 2,6-$Me_2C_6H_3$Br. It is seen that PhBr is evidently more reactive than 2,6-$Me_2C_6H_3$Br in the catalytic system. This reactivity order is opposite of that observed in stoichiometric systems (entries 1 and 3 in Table 2), indicating that the rate of catalytic reaction is controlled by an elementary process other than step b in Scheme 1: presumably the oxidative addition step a.

CONCLUSION

It has been found that the complexes [PdAr(μ-O_2CR)(PPh_3)]$_n$ (**1**), bearing PPh_3 and μ-carboxylate ligands, are sufficiently reactive toward 2-methylthiophene (**2**), affording the corresponding direct arylation products **3** in high yields. Although complexes **1** adopt a dimeric or tetrameric structure in the solid state, they are interconverted with the monomeric species [PdAr(O_2CR-κ^2O)(PPh_3)] (**5**) in solution. Since the higher

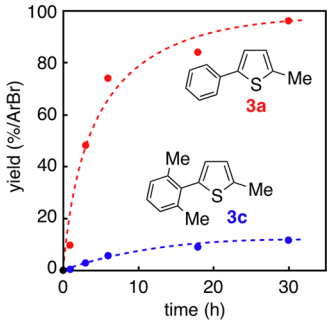


Figure 5. Catalytic direct arylation of 2-methylthiophene (**2**, 1.0 mmol) with PhBr (0.5 mmol) and 2,6-$Me_2C_6H_3$Br (0.5 mmol) in DMA (1.0 mL) in the presence of **1a** (0.010 mmol) and K_2CO_3 (1.0 mmol) at 90 °C.

content of **5** tends to provide the higher reactivity toward **2**, it is reasonable that **5** reacts with **2** to give **3**. These observations are consistent with the CMD pathway, which has been proposed by theoretical studies,[4,5] but so far scarcely reproduced by experimental studies using isolated arylpalladium complexes.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Nitrogen was dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.62 MHz, ^{19}F NMR 376.46 MHz, and ^{31}P NMR 161.97 MHz). Chemical shifts are reported in δ (ppm), referenced to ^{1}H (residual) and ^{13}C signals of deuterated solvents as internal standards or to the ^{19}F signal of C_6F_6 (δ −163.0) and the ^{31}P signal of 85% H_3PO_4 (δ 0.0) as external standards. Elemental analysis was performed by ICR Analytical Laboratory, Kyoto University. IR spectra were recorded on a JASCO FT/IR-410 or FT/IR-4100 spectrometer in a KBr pellet or a NaCl cell (path length = 0.1 cm). Analytical HPLC was carried out on a JASCO HPLC assembly consisting of a PU-2080 Plus pump, a model RI-1530 refractive index detector, and an Intersil ODS-P column (CH_3CN/H_2O = 3:2 v/v). GLC analysis was performed on a Shimadzu GC-2025 instrument equipped with a FID detector and a CBP-1 capillary column (25 m × 0.25 mm). Mass spectra were measured on a Shimadzu GC-MS QP2010 spectrometer (EI, 70 eV).

Toluene (Kanto, dehydrated), and CH_2Cl_2, Et_2O, and THF (Wako, dehydrated) were used as received. 1,4-Dioxane and DMA were dried over Na/Ph_2CO and CaH_2, respectively, distilled, and stored over activated MS4A. 2-Methylthiophene and bromoarenes were distilled after passing through a short pad of activated alumina. K_2CO_3 was dried overnight at 120 °C under vacuum and handled in a glovebox. [$PdCl_2(PPh_3)_2$],[16] [PdPh(μ-OH)(PPh_3)]$_2$,[17] [Pd(2-MeC_6H_4)(μ-OH)(PPh_3)]$_2$,[18] [PdPh(μ-O_2CMe)(PPh_3)]$_2$ (**1a**),[10] [PdPh(O_2CMe)-(PPh_3)$_2$] (**4a**),[19] [PdPh(μ-I)(PPh_3)]$_2$,[17] and 5-phenyl-2-methylthiophene (**3a**)[20] were prepared according to the literature. All other chemicals were obtained from commercial suppliers and used without further purification.

Synthesis of [Pd(2,6-$Me_2C_6H_3$)(μ-OH)(PPh_3)]$_2$. This complex was prepared according to the procedure for [PdPh(μ-OH)-(PPh_3)]$_2$.[17] A mixture of [$PdCl_2(PPh_3)_2$] (1.43 g, 2.0 mmol), 2,6-dimethyliodobenzene (500 μL, 3.4 mmol), a 25 M aqueous solution of KOH (2 mL), and benzene (40 mL) was stirred under reflux for 6 days. After water (50 mL) and benzene (50 mL) were added to the hot heterogeneous solution, the organic layer was separated, and the aqueous phase was washed with benzene (3 × 60 mL). The combined benzene solution was filtered through a Celite pad, and the filtrate was concentrated to afford a yellow oil, which was sonicated in acetone (40 mL) to afford a white solid. The solid was collected by filtration, washed with acetone, and dried under vacuum to afford a mixture of

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$[Pd(2,6\text{-}Me_2C_6H_3)(\mu\text{-}OH)(PPh_3)]_2$ (56%) and $[Pd(2,6\text{-}Me_2C_6H_3)(\mu\text{-}I)(PPh_3)]_2$ (4%) (600 mg, 60% in total), which was employed for the synthesis of **1c** without separation. The identification data for $[Pd(2,6\text{-}Me_2C_6H_3)(\mu\text{-}OH)(PPh_3)]_2$ are as follows. ^{1}H NMR (CD_2Cl_2): δ −1.82 (d, J = 2.8 Hz, 2H, OH), 2.61 (s, 12H, CH_3), 6.43 (d, J = 7.6 Hz, 4H, $H^{3,5}$ of C_6H_3), 6.57 (t, J = 7.6 Hz, 2H, H^4 of C_6H_3), 7.21 (dt, J = 7.6, 2.0 Hz, 12H, $H^{2,6}$ of Ph), 7.31−7.39 (m, 18H, $H^{3,4,5}$ of Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.0 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 26.8 (d, J = 4 Hz, CH_3), 124.1 (s, C^4 of C_6H_3), 125.6 (s, $C^{3,5}$ of C_6H_3), 128.6 (d, J = 11 Hz, $C^{3,5}$ of Ph), 130.8 (d, J = 1 Hz, C^4 of Ph), 131.9 (d, J = 48 Hz, C^1 of Ph), 134.6 (d, J = 12 Hz, $C^{2,6}$ of Ph), 142.0 (d, J = 2 Hz, $C^{2,6}$ of C_6H_3), 153.0 (d, J = 6 Hz, C^1 of C_6H_3). Anal. Calcd for $0.93C_{52}H_{50}O_2P_2Pd_2{\cdot}0.07C_{52}H_{48}I_2P_2Pd_2$: C, 62.63; H, 5.05. Found: C, 62.82; H, 5.10.

Synthesis of $[PdPh(\mu\text{-}O_2C^tBu)(PPh_3)]_2$ (1d). This complex was prepared according to the procedure for $[PdPh(\mu\text{-}O_2CMe)(PPh_3)]_2$.[10] A mixture of $[PdPh(\mu\text{-}OH)(PPh_3)]_2$ (90.3 mg, 0.10 mmol), pivalic acid (38.1 mg, 0.37 mmol), and benzene (5 mL) was stirred at room temperature for 10 min to afford a pale yellow solution. The solvent was removed, and the residue was dissolved in CH_2Cl_2 (5 mL), diluted with hexane (20 mL), and allowed to stand at −20 °C to afford pale yellow crystals of **1d**, which were collected by filtration, washed with cold Et_2O, and dried under vacuum (35.6 mg, 32%). The complexes $[Pd(2\text{-}MeC_6H_4)(\mu\text{-}O_2CMe)(PPh_3)]_2$ (**1b**) and $[Pd(2,6\text{-}Me_2C_6H_3)(\mu\text{-}O_2CMe)(PPh_3)]_4$ (**1c**) were similarly prepared using $[Pd(2\text{-}MeC_6H_4)(\mu\text{-}OH)(PPh_3)]_2$ and $[Pd(2,6\text{-}Me_2C_6H_3)(\mu\text{-}OH)(PPh_3)]_2$ instead of $[PdPh(\mu\text{-}OH)(PPh_3)]_2$, and acetic acid instead of pivalic acid, respectively.

1b: 61% yield. ^{1}H NMR (CD_2Cl_2): δ 1.80 (br, 6H, O_2CCH_3), 2.10−2.72 (brm, 6H, $CH_3C_6H_4$), 6.30−6.60, 6.61−6.88, 6.90−7.52 (brm, 38H in total, Ph and C_6H_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 32.0 (br), 29.6 (br). IR (CH_2Cl_2): 1581, 1517, 1450, 1416 cm^{-1} (ν_{CO2}). IR (KBr): 1581, 1417 cm^{-1} (ν_{CO2}). Anal. Calcd for $C_{54}H_{50}O_4P_2Pd_2{\cdot}0.5H_2O$; C, 61.96; H, 4.91. Found: C, 61.82; H, 4.86.

1c: 47% yield. ^{1}H NMR (CD_2Cl_2): δ 1.90 (br, 12H, O_2CCH_3), 2.41 (br, 24H, $(CH_3)_2C_6H_3$), 6.44 (d, J = 7.3 Hz, 8H, $H^{3,5}$ of C_6H_3), 6.65 (t, J = 7.3 Hz, 4H, H^4 of C_6H_3), 7.23−7.31, 7.36−7.45 (m, 60H in total, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.2 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 24.8 (brs, O_2CCH_3), 25.7 (brs, $(CH_3)_2C_6H_3$), 125.0 (s, C^4 of C_6H_3), 126.4 (s, $C^{3,5}$ of C_6H_3), 128.9 (d, J = 11 Hz, $C^{3,5}$ of Ph), 130.8 (d, J = 52 Hz, C^1 of Ph), 131.3 (s, C^4 of Ph), 134.8 (d, J = 12 Hz, $C^{2,6}$ of Ph), 140.9 (s, $C^{2,6}$ of C_6H_3), 150.0 (s, C^1 of C_6H_3). IR (CH_2Cl_2): 1550, 1515, 1449, 1413 cm^{-1} (ν_{CO2}). IR (KBr): 1547, 1412 cm^{-1} (ν_{CO2}). Anal. Calcd for $C_{112}H_{108}O_8P_4Pd_4$: C, 63.11; H, 5.10. Found: C, 62.82; H, 5.10.

1d: ^{1}H NMR (CD_2Cl_2): δ 0.62 (s, 15.3H, $C(CH_3)_3$), 1.17 (s, 2.7H, $C(CH_3)_3$), 6.67−6.74, 6.77−6.84, 6.91−6.96 (m, 10H in total, PdPh), 7.02−7.10, 7.20−7.31, 7.33−7.40, 7.43−7.51 (m, 30H in total, PPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.7 (s, 1.7P), 32.2 (s, 0.30P). IR (CH_2Cl_2): 1577, 1415 cm^{-1} (ν_{CO2}). IR (KBr): 1577, 1414 cm^{-1} (ν_{CO2}). Anal. Calcd for $C_{58}H_{58}O_4P_2Pd_2{\cdot}CH_2Cl_2$: C, 60.11: H, 5.13. Found: C, 60.34; H, 5.36.

Synthesis of $[PdPh(\mu\text{-}O_2CCF_3)(PPh_3)]_2$ (1e). To a suspension of $[PdPh(\mu\text{-}OH)(PPh_3)]_2$ (92.2 mg, 0.10 mmol) in toluene (4 mL) at −78 °C was added trifluoroacetic acid (23 μL, 0.30 mmol). After stirring the mixture for a few minutes, Et_2O (15 mL) was added at the same temperature to precipitate a white solid, which was collected by filtration, washed with cold Et_2O, and dried under vacuum (37.5 mg, 34%). ^{1}H NMR (CD_2Cl_2): δ 6.74−6.80 (m, 6H, $H^{2,4,6}$ of PdPh), 6.94 (t, J = 7.2 Hz, 4H, $H^{3,5}$ of PdPh), 7.11−7.17, 7.18−7.27, 7.33−7.40 (m, 60H in total, PPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.1 (s). ^{19}F NMR (CD_2Cl_2): δ −75.3 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 116.5 (q, J = 287 Hz, CF_3), 124.9 (s, C^4 of PdPh), 128.1 (d, J = 3 Hz, $C^{3,5}$ of PdPh), 128.9 (d, J = 11 Hz, $C^{3,5}$ of PPh), 129.3 (d, J = 54 Hz, C^1 of PPh), 131.3 (d, J = 2 Hz, C^4 of PPh), 135.0 (d, J = 12 Hz, $C^{2,6}$ of PPh), 137.3 (d, J = 3 Hz, $C^{2,6}$ of PdPh), 145.9 (s, C^1 of PdPh), 164.3 (q, J = 38 Hz, CO_2). IR (CH_2Cl_2): 1563, 1434 cm^{-1} (ν_{CO2}). IR (KBr): 1562, 1434 cm^{-1} (ν_{CO2}). Anal. Calcd for $C_{52}H_{40}F_6O_4P_2Pd_2$: C, 55.88; H 3.61. Found: C, 55.98; H, 3.87.

Reaction of $[PdPh(\mu\text{-}O_2CMe)(PPh_3)]_2$ (1a) with 2-Methylthiophene (2) (Scheme 2 and Table 1). A typical procedure for the experiments in Scheme 1 and Table 1 is as follows. Complex **1a** (10.1 mg, 0.010 mmol) and C_6Me_6 (4.1 mg, 0.025 mmol; internal standard) were placed in an NMR sample tube equipped with a Teflon screw valve, and 1,4-dioxane (0.50 mL) and 2-methylthiophene (**2**; 39 μL, 0.40 mmol) were added at room temperature. The solution was degassed three times by freeze−pump−thaw cycles. The sample tube was placed in an oil bath controlled to 90 °C. The reaction was followed at intervals by $^{31}P\{^1H\}$ NMR spectroscopy using the following marker signals: **1a** (δ 30.7), $[PdPh(O_2CMe)(PPh_3)_2]$ (**4a**; δ 21.9). After complete consumption of **1a**, the coupling product (**3a**) and biphenyl were analyzed by GC-MS and HPLC. The solution was concentrated to dryness, dissolved in CD_2Cl_2 (0.5 mL), and analyzed by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. The amount of **4a** was determined by ^{1}H NMR spectroscopy using the following marker signals: C_6Me_6 (δ 2.20), **4a** (δ 6.56). The NMR data of **4a** were identical to those reported.[18] ^{1}H NMR (CD_2Cl_2): δ 0.87 (s, 3H, CH_3), 6.31 (virtual triplet, J = 7.2 Hz, 2H, $H^{3,5}$ of PdPh), 6.52 (d, 1H, J = 7.2 Hz, H^4 of PdPh), 6.56 (d, 2H, J = 7.6 Hz, $H^{2,6}$ of PdPh), 7.28 (virtual triplet, J = 7.6 Hz, 12H, $H^{2,6}$ of PPh), 7.36 (d, 6H, J = 7.2 Hz, H^4 of PPh), 7.40 (br, 12H, $H^{3,5}$ of PPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.2 (s).

Kinetic Examinations for the Reaction of $[PdPh(\mu\text{-}O_2CMe)(PPh_3)]_2$ (1a) with 2-Methylthiophene (2) (Figures 1 and 2). A typical procedure is as follows. To a 10 mL Schlenk tube containing complex **1a** (40.4 mg, 0.040 mmol) and C_6Me_6 (16.3 mg, 0.10 mmol; internal standard) were added successively 1,4-dioxane (2.0 mL) and **2** (155 μL, 1.60 mmol). The resulting solution (total volume = 2.2 mL) was degassed three times by freeze−pump−thaw cycles. The solution was stirred at 90 °C under a nitrogen atmosphere. The amounts of 5-phenyl-2-methylthiophene (**3a**) and biphenyl produced at intervals were followed by HPLC.

Reactions of $[PdAr(\mu\text{-}O_2CR)(PPh_3)]_n$ (1) with 2-Methylthiophene (2) (Table 2). A typical procedure is as follows (entry 1). Complex **1a** (8.1 mg, 0.0080 mmol) and C_6Me_6 (3.2 mg, 0.020 mmol; internal standard) were placed in an NMR sample tube equipped with a Teflon screw valve, and THF (0.40 mL) and 2-methylthiophene (**2**; 31 μL, 0.32 mmol) were added at room temperature. The mixture was degassed three times by freeze−pump−thaw cycles and heated at 40 °C to dissolve **1a**. A capillary containing a solution of $PPh_2(C_6H_4\text{-}2\text{-}OMe)$ (40 mM) in toluene-d_8 was loaded into the NMR sample tube as an internal standard. The system was again degassed three times by freeze−pump−thaw cycles and placed in an NMR sample probe controlled to 65.0 ± 0.1 °C. The reaction was examined at intervals by $^{31}P\{^1H\}$ NMR spectroscopy using the following marker signals: **1a** (δ 30.7), **4a** (δ 22.0), $PPh_2(C_6H_4\text{-}2\text{-}OMe)$ (δ −13.9). After complete consumption of **1a**, organic products formed in the system (**3a** and biphenyl) were analyzed by GC-MS and HPLC.

Catalytic Direct Arylation of 2-Methylthiophene (2) with Aryl Bromides. To a 10 mL Schlenk tube containing complex **1a** (10.1 mg, 0.010 mmol), K_2CO_3 (138 mg, 1.0 mmol), and C_6Me_6 (8.1 mg, 0.050 mmol; internal standard) were added successively DMA (0.50 mL), **2** (97 μL, 1.0 mmol), bromobenzene (53 μL, 0.50 mmol), and 2,6-dimethylbromobenzene (67 μL, 0.50 mmol). The solution was degassed three times by freeze−pump−thaw cycles. The mixture was stirred at 90 °C, and the amounts of the 5-phenyl-2-methylthiophene (**3a**) and 2-methyl-5-(2,6-dimethylphenyl)thiophene (**3c**) produced at intervals were followed by GLC.

X-ray Structural Analysis. Single crystals of **1b−d** suitable for X-ray diffraction study were grown by slow diffusion of pentane (**1b**) or hexane (**1c**, **1d**) into CH_2Cl_2 solutions at −20 °C. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The intensity data were collected at 173 K and corrected for Lorentz and polarization effects and for absorption. The structures were solved by heavy atom Patterson methods (PATTY), expanded using Fourier techniques (DIRDIF99),[21] and refined on F^2 for all reflections (SHELXL-97).[22] Non-hydrogen atoms, except for the oxygen atom of crystal water in **1b**, were refined anisotropically. Hydrogen atoms were

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placed at calculated positions using AFIX instructions. The molecular structures are given in Figure 4 (**1d**) and Figure S1 (**1b**) and Figure S2 (**1c**) in Supporting Information. Selected bond distances and angles are listed in Table S1. The crystal data and the summary of data collection and refinement are listed in Table S2.

DFT Calculations for IR Assignments. Geometry optimization for model compounds were carried out for **1a** (**1a′**: [PdPh(μ-O_2CMe)(PH_3)]$_2$), **5a** (**5a′**: [PdPh(O_2CMe-κ^2O)(PH_3)]), **1c** (**1c′**: [Pd(2,6-$Me_2C_6H_3$)(μ-O_2CMe)(PH_3)]$_4$), and **5c** (**5c′**: [Pd(2,6-$Me_2C_6H_3$)(O_2CMe-κ^2O)(PH_3)]). All calculations were performed without any symmetry constraints using the B3LYP level of density functional theory.[23] The Gaussian 03 program package was used for all calculations.[24] The Pd atom was described using the LANL2DZ basis set including a double-ζ basis set with the Hay and Wadt effective core potential.[25] The 6-31G(d) basis set was used for other atoms.[26] The optimized geometry of **1a′**, **5a′**, and **5c′** exhibited no imaginary frequency, while the optimized geometry of **1c′** exhibited one small imaginary frequency (−15.44i cm^{-1}). The calculated vibrational frequencies were scaled by 0.9613, which is customary for the B3LYP method.[27] Calculated vibrational wavenumbers are summarized in Table S3. The calculated data are consistent with the experimental values given in Table 3. The Cartesian coordinates of model compounds are reported in Tables S4−S7.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic and computational details and crystallographic data (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Prof. Robert H. Grubbs (Caltech) on the occasion of his 70th birthday.

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