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Electrophilic Substitution of Thiophenes with Arylpalladium(II) and Platinum(II) Complexes: Mechanistic Studies on Palladium-Catalyzed CH Arylation of Thiophenes

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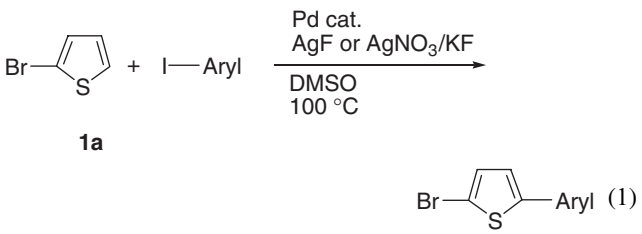
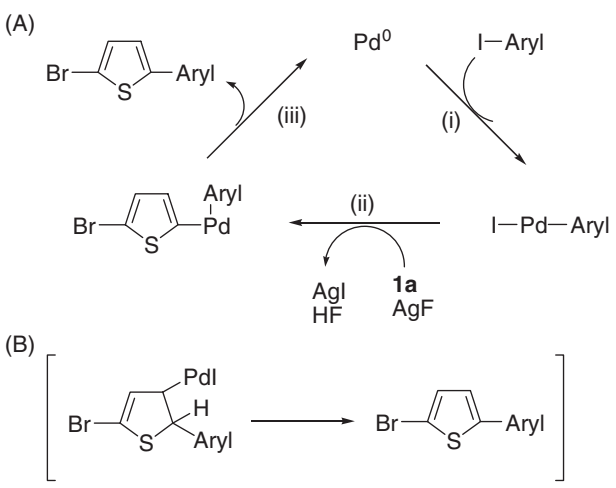
Mechanistic studies on palladium-catalyzed CH arylation of thiophenes which has been shown by our group are carried out by a stoichiometric reaction of organometallic complexes. The reaction of arylpalladium(II) halide with 2,3-dibromothiophene in the presence of $AgNO_3$/KF as an activator induces electrophilic substitution at the CH bond of the thiophene to give CH arylated product. The similar reaction of arylplatinum(II) halide with thiophene derivatives affords the aryl(thienyl)platinum(II) complex which is an analog of a precursor of the product of the CH arylation reaction. These results suggest that the palladium-catalyzed CH arylation reaction of thiophenes proceeds through electrophilic substitution.

Transition-metal-catalyzed CH functionalization[1,2] attracts considerable attention as an alternative and more straightforward pathway to form a carbon–carbon bond compared to transition-metal-catalyzed coupling of aryl halides with organometallic reagents.[3] In particular, CH substitution reactions of heteroaromatic compounds increase their significance since compounds bearing a heteroaromatic moiety are promising for advanced materials such as organic thin film transistors (TFTs) and light-emitting devices.[4] In order to develop further practical and efficient catalytic CH substitution reactions, mechanistic understanding of the reaction is very important.

We have shown that CH arylation of 2-bromothiophene (**1a**) with aryl iodide takes place in the presence of a palladium catalyst and AgF or $AgNO_3$/KF to give aryl(bromo)thiophene.[5] It is noteworthy that the catalytic reaction of bromothiophene proceeds smoothly with the carbon–bromine bond remaining intact (eq 1).



A plausible reaction mechanism for the CH arylation reaction is shown in Scheme 1A:[1d,5] (i) The reaction of Pd^0 with aryl iodide forms aryl–Pd^{II}–I. (ii) The reaction of aryl–Pd^{II}–I with **1a** gives aryl(thienyl)palladium(II) complex through electrophilic substitution at the CH bond. (iii) Reductive elimination of aryl(bromo)thiophene from aryl(thienyl)palladium(II) complex takes place accompanied by the regeneration of palladium(0). Step (i) is well known to occur with a variety of palladium(0) complexes and aryl halides and reductive elimination of $Aryl^1$–$Aryl^2$ is also known



Scheme 1. Plausible reaction mechanisms of palladium-catalyzed CH arylation of bromothiophene. (A) Electrophilic substitution followed by reductive elimination and (B) Mizoroki–Heck type reaction mechanism.

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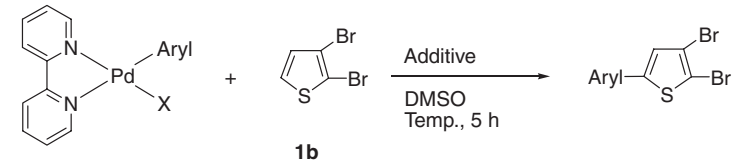
Table 1. The Reaction of Aryl(bpy)halopalladium(II) with 2,3-Dibromothiophene (**1b**)[a)]



1b

2a: Aryl = -C_6H_3-Me_2-3,5, X = I;
2b: Aryl = -C_6H_4-COOEt-4, X = I;
2c: Aryl = -C_6H_3-$(CF_3)_2$-3,5, X = I;
3a: Aryl = -C_6H_3-Me_2-3,5, X = Br;
4a: Aryl = -C_6H_3-Me_2-3,5, X = Cl;

5ab: Aryl = -C_6H_3-Me_2-3,5
5bb: Aryl = -C_6H_4-COOEt-4
5bc: Aryl = -C_6H_3-$(CF_3)_2$-3,5

Pd complex	Temp/°C	Additive	Product (yield/%)	Recovered Pd complex/%
2a	50	$AgNO_3$/KF	**5ab** (71)	—
2a	50	None	**5ab** (0)	51
2a	50	KF	**5ab** (0)	58
2a	50	$AgNO_3$	**5ab** (0)	—
2a	rt	$AgNO_3$/KF	**5ab** (67)	—
2b	rt	$AgNO_3$/KF	**5bb** (66)	—
2c	rt	$AgNO_3$/KF	**5cb** (64)	—
3a	rt	$AgNO_3$/KF	**5ab** (55)	—
4a	rt	$AgNO_3$/KF	**5ab** (52)	—

a) The reaction was carried out with aryl(bpy)halopalladium(II) (0.05 mmol) and 2,3-dibromothiophene (**1b**) (0.12 mmol) in the presence of additive (0.2 mmol) in DMSO for 5 h.

to proceed from $Aryl^1$–Pd–$Aryl^2$ (iii).[6] On the other hand, the step reaction (ii) has not been well studied and details of this reaction have not yet been clear. The other plausible mechanism is shown in Scheme 1B which involves insertion of a C=C bond of thiophene into the Pd–Aryl bond and successive β-hydrogen elimination (Mizoroki–Heck type reaction).[7] We have confirmed the formation of AgI through powder XRD analysis of the silver residue after the catalytic reaction.[5a] However, neither isolation nor detection of the important intermediate aryl(thienyl)palladium(II) complex, which would be strong evidence to support the mechanism, has been achieved yet. The reaction mechanism of the palladium-catalyzed CH arylation would be clear if aryl(thienyl)palladium(II) complex is detected and characterized.

Herein, we report studies on a stoichiometric reaction of palladium and platinum complexes with thiophene derivatives for the purpose of obtaining intermediate metal complexes of a step reaction of catalytic CH arylation.[8]

Results and Discussion

We synthesized aryl(bpy)iodopalladium(II) (bpy = 2,2′-bipyridine) **2a**–**2c** by oxidative addition of aryl iodide to bis(dibenzylideneacetone)palladium(0) in the presence of bidentate nitrogen donor ligand in a manner reported previously.[9] Aryl(bpy)bromopalladium(II) **3a** (Aryl = –C_6H_3–Me_2-3,5) and aryl(bpy)chloropalladium(II) **4a** (aryl = –C_6H_3–Me_2-3,5) were also prepared by the reaction of **2a** (aryl = –C_6H_3–Me_2-3,5) with $AgNO_3$ and aqueous solution of KBr or NaCl according to the literature.[10] Since aryl(halo)palladium(II) complexes were in hand, a stoichiometric reaction of aryl(halo)palladium(II) complex with thiophene derivatives in the presence of $AgNO_3$/KF was carried out. As the substrate, 2,3-dibromothiophene (**1b**), which resulted in the highest yield in the catalytic CH arylation reaction, was employed. The reaction was performed under several conditions with aryl(bpy)halopalladium(II) **2a**–**2c**, **3a**, or **4a** and 2.4 equivalents of 2,3-dibromothiophene (**1b**) in DMSO for 5 h.[5b] The results are summarized in Table 1.

Treatment of palladium complex **2a** and **1b** with $AgNO_3$/KF at 50 °C afforded the corresponding coupling product **5ab** in 71% yield, while the reaction in the absence of $AgNO_3$ and KF did not proceed but led to recovered complex **2a** in 51% yield. In addition, recovery of complex **2a** was observed in 58% yield in the presence of KF and in the absence of $AgNO_3$. Although consumption of complex **2a** was observed, the reaction with $AgNO_3$ (in the absence of KF) afforded no coupling product, but gave unidentified compounds bearing neither thienyl–palladium nor thienyl–aryl bonds. It is noteworthy that the reaction proceeded at room temperature although the catalytic CH arylation of thiophene required 50–100 °C. The reaction with other aryl(iodo)palladium(II) complexes like (bpy)(4-ethoxycarbonylphenyl)iodopalladium(II) (**2b**) and [3,5-bis(trifluoromethyl)phenyl](bpy)iodopalladium(II) (**2c**) with **1b** in the presence of $AgNO_3$/KF similarly proceeded to give **5bb** and **5cb**, respectively. When arylpalladium(II) bromide **3a** was treated with **1b** and $AgNO_3$/KF at room temperature for 5 h, arylthiophene **5ab** was also obtained in 55% yield. The reaction of arylpalladium(II) chloride **4a** also proceeded to afford **5ab** in 52% yield.

Since the catalytic CH arylation is considered to proceed through an aryl–Pd^{II}–I complex, the reaction of palladium complexes **2a**–**2c** with **1b** should be a part of the catalytic cycle, which is a class of electrophilic substitution of **1b** with aryl–Pd^{II}–I leading to the aryl(thienyl)palladium complex. However, aryl(thienyl)palladium(II) was not obtained by the reaction of **2a** and **1b** at room temperature. Because reductive elimination of biaryl from diarylpalladium(II) complexes is known to occur smoothly under mild conditions, the aryl(thienyl)palladium complex once formed would be immedi-

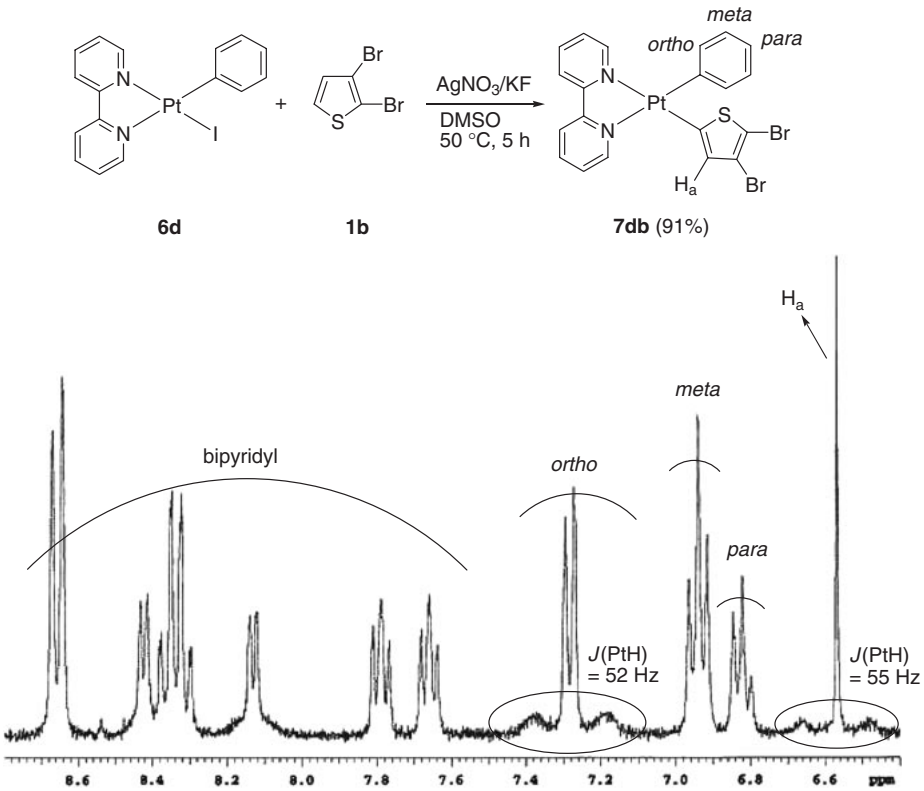


Figure 1. Synthesis of platinum(II) complex **7db** and its ^{1}H NMR spectrum of platinum(II) complex **7db** (300 MHz, DMSO-d_6, rt).

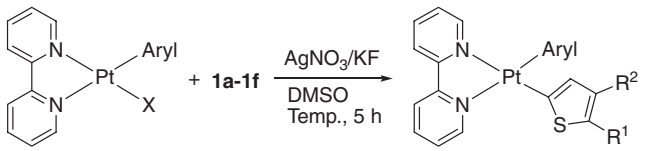
ately converted to the product **5ab** through reductive elimination.[11] Though the palladium complex was switched to that bearing an electron-withdrawing group **2b** (Aryl = –C_6H_4–COOEt-4) or **2c** (Aryl = –C_6H_3–$(CF_3)_2$-3,5) and the reaction temperature was controlled at room temperature in order to retard reductive elimination, neither isolation nor detection of the complex was successful. Accordingly, the results suggest that reductive elimination is inevitable in the electrophilic substitution of 2,3-dibromothiophene (**1b**). The results also indicate that the $AgNO_3$/KF system serves as an effective activator in electrophilic substitution of aryl–Pd^{II}–I, where both $AgNO_3$ and KF are necessary for the reaction to take place. Although the role of the $AgNO_3$/KF system as an activator has not been clear yet, strong affinity between silver and halogen atoms as well as the effect of fluoride ion would be a key for the reaction. Although the available aryl halide in the catalytic CH arylation reaction of thiophene has been limited to the iodide,[5] bromo and chloro palladium complex **3a** and **4a** underwent the CH substitution reaction. These findings suggest that the catalytic CH arylation of a thiophene derivative with an aryl bromide or chloride would be possible under appropriate conditions that allow oxidative addition of the aryl halide to Pd^0. Further development of the catalytic CH arylation by the design of highly active catalysts will be studied in due course.

Since aryl(thienyl)palladium(II) complex was not detected in the stoichiometric reaction with thiophene derivatives, we envisaged to synthesize its platinum analog, which would be more stable toward reductive elimination. The reaction of (bpy)(iodo)phenylplatinum(II) (**6d**)[12] with 2,3-dibromothiophene (**1b**) was first examined with $AgNO_3$/KF as an activator under conditions similar to those carried out in the reaction of the corresponding palladium complex and found to afford (bpy)(phenyl)thienylplatinum(II) **7db** in 91% yield (Figure 1). The ^{1}H NMR spectrum of **7db** showed a doublet signal at 7.28 ppm corresponding to 2H of the *ortho*-phenyl signal, which accompanied the coupling by ^{195}Pt nuclei (^{3}J(PtH) = 52 Hz) indicating the existence of a Pt–C(phenyl) bond.[12] In addition, a singlet signal at 6.57 ppm, which corresponds to the β-proton of the thiophene ring, was observed along with the satellite of ^{195}Pt (^{3}J(PtH) = 55 Hz). These results suggest that **7db** possesses both Pt–C(phenyl) and Pt–C(thienyl) bonds.

Worthy of note is that this is a new class of reactivity in platinum(II) complexes[13] to construct a Pt–C σ bond by intermolecular electrophilic substitution with a heteroaromatic compound in the presence of $AgNO_3$/KF without participation of proximal chelation by a heteroatom.[14] It should also be pointed out that the platinum–carbon bond formation occurred smoothly at the CH bond when the thiophene derivative had a carbon–bromine bond. This kind of aryl(thienyl)platinum(II) complex bearing a carbon–bromine bond on the thiophene ring has hardly been synthesized by other synthetic pathways, to the best of our knowledge, such as nucleophilic substitution on the platinum metal with a thienyl metallic reagent.[15]

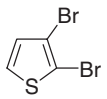
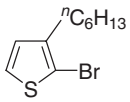
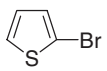
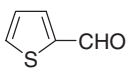
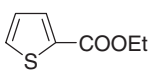
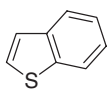
As summarized in Table 2, the reaction with several platinum complexes and a variety of thiophene derivatives was examined. A platinum complex bearing a phenyl or 4-methylphenyl group was employed for the reaction with thiophenes. The iodo(phenyl)platinum(II) complex **6d** reacted with 2,3-dibromothiophene (**1b**) even at room temperature to afford the corresponding aryl(thienyl)platinum complex **7db** in a slightly inferior yield (86%). In addition to **1b**, 2-bromo-3-hexylthiophene (**1c**) also afforded the aryl(thienyl)platinum complex **7dc**

Table 2. The Reaction of [PtX(Aryl)(bpy)] **6d** and **6e** with Thiophene Derivatives[a)]



6d: Aryl = -C_6H_5, X = I;
6e: Aryl = -C_6H_4-Me-4, X = Cl

7db: Aryl = -C_6H_5, R^1 = R^2 = Br;
7dc: Aryl = -C_6H_5, R^1 = Br, R^2 = -$^nC_6H_{13}$;
7eb: Aryl = -C_6H_4-Me-4, R^1 = R^2 = Br;
7ea: Aryl = -C_6H_4-Me-4, R^1 = Br, R^2 = H;
7ed: Aryl = -C_6H_4-Me-4, R^1 = CHO, R^2 = H;
7ee: Aryl = -C_6H_4-Me-4, R^1 = COOEt, R^2 = H;
7ef: Aryl = -C_6H_4-Me-4, R^1, R^2 = -CH=CH-CH=CH-

Pt complex	Thiophene	Temp/°C	Product	Yield/%
6d	 **1b**	rt	**7db**	86
6d	 **1c**	50	**7dc**	87
6e	**1b**	50	**7eb**	74
6e	 **1a**	50	**7ea**	65
6e	 **1d**	50	**7ed**	73
6e	 **1e**	50	**7ee**	74
6e	 **1f**	50	**7ef**	78

a) The reaction was carried out with [PtX(Aryl)(bpy)] (0.05 mmol) and thiophene derivative (0.12 mmol) for 5 h in the presence of $AgNO_3$ (0.2 mmol) and KF (0.2 mmol) in DMSO.

in 87% yield after stirring at 50 °C for 5 h. The reaction of (bpy)chloro(4-methylphenyl)platinum(II) (**6e**) with thiophene derivative was also found to proceed. The corresponding platinum complexes were obtained by the reaction with several thiophene derivatives bearing a bromo group at the 2-position (**1a** and **1b**) and an electron-withdrawing group (**1d** and **1e**). The corresponding complexes **7ea**–**7ee** were obtained in good to excellent yields. Benzothiophene (**1f**) also underwent the reaction with platinum complex **6e** to afford **7ef** in 78% yield.

Aryl(thienyl)platinum(II) complex **7ee** was isolated as a single crystal and characterized by X-ray crystallography. Figure 2 depicts the molecular structure of **7ee** with a square-planar coordination around the Pt center. The thienyl ligand bonds to the platinum center through its α-carbon (Pt(1)–C(1) = 1.989(6) Å).

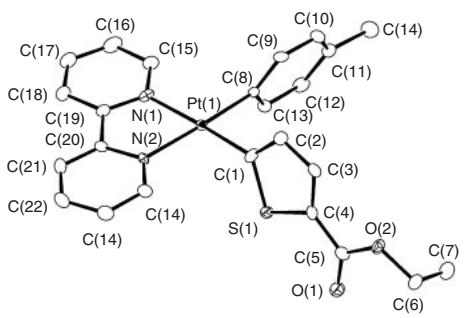
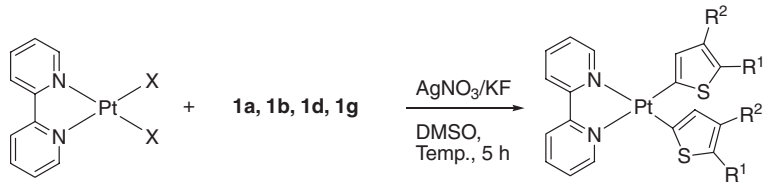
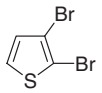
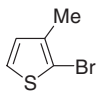
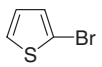
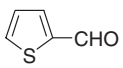


Figure 2. ORTEP drawing of **7ee** (50% probability). Hydrogen atoms were omitted for clarity.

Table 3. Reaction of $[PtX_2(bpy)]$ with Thiophene Derivatives[a)]

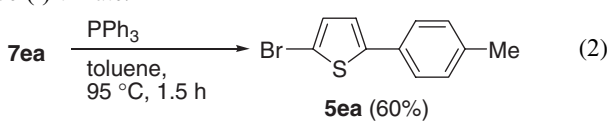


8a: R^1 = Br, R^2 = H;
8b: R^1 = Br, R^2 = Br;
8d: R^1 = CHO, R^2 = H;
8g: R^1 = Br, R^2 = Me;

Pt complex	Thiophene	Temp/°C	Product	Yield/%
$[PtI_2(bpy)]$	 **1b**	50	**8b**	70
$[PtCl_2(bpy)]$	**1b**	50	**8b**	65
$[PtI_2(bpy)]$[b)]	 **1g**	50	**8g**	79
$[PtI_2(bpy)]$[b)]	**1g**	rt	**8g**	10
$[PtCl_2(bpy)]$	 **1a**	50	**8a**	53
$[PtCl_2(bpy)]$	 **1d**	50	**8d**	69

a) Unless noted, the reaction was carried out with $[PtX_2(bpy)]$ (0.1 mmol) and thiophene derivative (0.3 mmol) for 5 h in the presence of $AgNO_3$ (0.5 mmol) and KF (0.5 mmol) in DMSO. b) The reaction was carried out with $[PtI_2(bpy)]$ (0.05 mmol), **1g** (0.24 mmol), $AgNO_3$ (0.4 mmol), and KF (0.4 mmol).

The reductive elimination of the arylthiophene **5db** from the obtained aryl(thienyl)platinum(II) complex **7db** was envisaged. Among several conditions to induce the reductive elimination step, no reaction was found to proceed by heating the complex **7db** at 100 °C for 17 h in DMSO-d_6. This finding suggests the high stability of the platinum complex bearing a thienyl ligand toward reductive elimination compared with other related diorganoplatinum(II) complexes.[16] Because complex **7db** showed high thermal stability, heating of **7db** with an additive was carried out to accelerate reductive elimination of **5db** according to the literature.[17] When a toluene solution of **7ea** and PPh_3 was heated at 95 °C for 1.5 h, corresponding arylthiophene **5ea**, which was considered to be generated by reductive elimination, was obtained in 60% yield (eq 2). By contrast, reductive elimination of **5db** was not observed by heating the complex **7db** with diethyl fumarate[18] or with silver(I) triflate.[15a]



(2)

The reaction of $[PtX_2(bpy)]$ (X = Cl and I)[12] was also found to proceed with thiophene through double electrophilic substitution.[2] The results are summarized in Table 3. Similar to the case of the reaction of aryl(halo)platinum(II) complexes **6d** and **6e**, the reaction of $[PtX_2(bpy)]$ (X = Cl and I) with 2,3-dibromothiophene (**1b**) in the presence of $AgNO_3$ and KF in DMSO at 50 °C afforded dithienylplatinum(II) complex **8b** in 70% yield (X = I) and 65% yield (X = Cl), respectively. Though the reaction of $[PtI_2(bpy)]$ with 2-bromo-3-methylthiophene (**1g**) at 50 °C afforded dithienylplatinum(II) complex **8g** in 79% yield, the reaction at room temperature gave **8g** in only 10% yield. This result was found to be in contrast to the reaction of aryl(halo)platinum(II) complexes **6d** and **6e**. The corresponding dithienylplatinum(II) complex was also obtained by the reaction with 2-bromothiophene (**1a**) and 2-formylthiophene (**1d**). The dithienylplatinum(II) complex is considered to be a platinum analog for the proposed intermediate of the homocoupling reaction catalyzed by palladium,[19] which is also suggested to proceed via electrophilic substitution of the dihalo complex with two equivalents of thiophene.

Conclusion

The reactions using stoichiometric amounts of palladium and platinum complexes were carried out to study the mechanism of catalytic CH arylation of thiophenes. When arylpalladium(II) halides **2a**–**2c** were treated with 2,3-dibromothiophene (**1b**), silver(I) nitrate, and potassium fluoride, the corresponding

arylthiophene, the product of CH arylation was obtained while aryl(thienyl)palladium(II) complex was not detected at all. On the other hand, aryl(thienyl)platinum(II) complex was synthesized by the similar reaction using arylplatinum(II) halides **6d** and **6e**. These findings strongly suggest that CH arylation of thiophenes with aryl iodide occurs by electrophilic substitution of the palladium complex promoted by the activating agent $AgNO_3$/KF. Based on the results of the reaction using arylpalladium bromide **3a** and chloride **4a**, aryl bromide and chloride may be applicable to the CH arylation of thiophene derivatives when appropriate reaction conditions are applied.

Experimental

General. Melting points were uncorrected. ^{1}H NMR (300 MHz, 500 MHz), ^{13}C NMR (75.5 MHz, 125 MHz) spectra were measured with a Varian Mercury 300 or Bruker Avance 500 spectrometer. Unless specified, measurements of the spectra were carried out with $CDCl_3$ as a solvent. The chemical shifts were expressed in ppm using $CHCl_3$ (7.26 ppm for ^{1}H) or DMSO-d_6 (2.49 ppm for ^{1}H) or $CDCl_3$ (77.0 ppm for ^{13}C) as an internal standard. IR spectra were recorded on Shimadzu FTIR-8100A. Elemental analysis was carried out with a LECO CHNS-932 CHNS or Yanaco MT-5 CHN autorecorder at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology. High-resolution mass spectra (HRMS, EI, or FAB) were measured with JEOL MStation.

Materials. DMSO was purchased from Wako Pure Chemical Industries, Co., Ltd. as an anhydrous grade and stored in a Schlenk tube under nitrogen atmosphere. Other chemicals were purchased and used as such. Preparation of palladium complex **2a**–**2c**, **3a**, and **4a** and platinum complexes **6d** and **6e** and [PtX_2(bpy)] (X = Cl and I) were performed by methods shown in the literature.[9,11–13]

General Procedure for the Reaction of Aryl(2,2′-bipyridine)iodopalladium(II) with 2,3-Dibromothiophene (1b) in the Presence of $AgNO_3$/KF. To a solution of [PdI(C_6H_4–COOEt-4)(bpy)] (**2b**, 24.7 mg, 0.05 mmol) in 3 mL of DMSO was added **1b** (0.014 mL, 0.12 mmol) under a nitrogen atmosphere. Potassium fluoride (11.6 mg, 0.2 mmol) and silver(I) nitrate (34 mg, 0.2 mmol) were then added. The resulting suspension was then stirred at room temperature for 5 h. The mixture was passed through a Celite pad, which was washed with dichloromethane repeatedly. The filtrate was washed with water twice. The organic layer was concentrated under reduced pressure to leave a crude oil. Purification by column chromatography on silica gel afforded 12.9 mg of **5bb** as light yellow solid (66%).

The reaction of **2a** and **2c** was carried out in a similar manner as above. The yield of **5ab** was estimated by ^{1}H NMR analysis using trichloroethene (6.46 ppm) as an internal standard on the basis of the characteristic signal at 7.08 ppm derived from proton at the 4-position of the thiophene ring, while that of **5cb** was determined by the proton signal of the 4-position of the phenyl ring (7.82 ppm).

General Procedure for the Reaction of Aryl(halo)platinum Complexes 6d and 6e with a Thiophene Derivative. To a mixture of [PtI(Ph)(bpy)] (**6d**, 27.8 mg, 0.05 mmol), 2,3-dibromothiophene (**1b**, 0.013 mL, 0.12 mmol), and potassium fluoride (11.6 mg, 0.2 mmol) was added $AgNO_3$ (34.0 mg, 0.2 mmol) in one portion under argon atmosphere. The resulting suspension was stirred at 50 °C for 5 h. After cooling to room temperature, the mixture was passed through a Celite pad, which was washed with dichloromethane repeatedly. The filtrate was washed with water twice. The organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by recrystallization to afford 30.5 mg of **7db** as a yellow solid (91%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.57 (s, 1H), 6.82 (m, 1H), 6.94 (m, 2H), 7.28 (m, 2H), 7.66 (ddd, J = 10.1, 7.5, 1.3 Hz, 1H), 7.79 (ddd, J = 10.1, 7.5, 1.6 Hz, 1H), 8.13 (dd, J = 7.5, 1.3 Hz, 1H), 8.30 (ddd, J = 10.4, 10.4, 2.0 Hz, 1H), 8.35 (ddd, J = 10.4, 10.4, 2.3 Hz, 1H), 8.42 (dd, J = 7.5, 1.6 Hz, 1H), 8.65 (d, J = 8.1 Hz, 2H). Anal. Calcd for $C_{20}H_{14}Br_2N_2PtS$: C, 35.89; H, 2.11; N, 4.19; S, 4.79%. Found: C, 36.12; H, 2.19; N, 4.07; S, 4.67%.

(2,2′-Bipyridine)[2-(5-bromo-4-hexylthienyl)]phenylplatinum(II) (7dc): ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.84 (t, J = 6.9 Hz, 3H), 1.27 (m, 6H), 1.51 (m, 2H), 2.41 (t, J = 7.8 Hz, 3H), 6.48 (s, 1H), 6.80 (m, 1H), 6.92 (m, 2H), 7.29 (m, 2H), 7.65 (ddd, J = 6.6, 6.5, 0.9 Hz, 1H), 7.73 (ddd, J = 6.6, 6.2, 1.2 Hz, 1H), 8.16 (dd, J = 5.1, 0.9 Hz, 1H), 8.32 (m, 2H), 8.42 (dd, J = 5.7, 0.9 Hz, 1H), 8.64 (d, J = 8.4 Hz, 2H); Anal. Calcd for $C_{26}H_{27}BrN_2PtS$: C, 46.29; H, 4.03; N, 4.15; S, 4.75%. Found: C, 45.80; H, 3.83; N, 4.20; S, 4.63%.

(2,2′-Bipyridine)[2-(5-bromothienyl)](4-methylphenyl)platinum(II) (7ea): ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.17 (s, 3H), 6.51 (d, J = 3.4 Hz, 1H), 6.75 (d, J = 7.5 Hz, 2H), 6.91 (d, J = 3.5 Hz, 1H), 7.16 (d, J = 7.9 Hz, 2H), 7.66 (ddd, J = 5.6, 5.7, 1.1 Hz, 1H), 7.74 (ddd, J = 5.5, 5.5, 1.0 Hz, 1H), 8.23 (dd, J = 5.6, 1.0 Hz, 1H), 8.29–8.34 (m, 2H), 8.44 (dd, J = 5.3, 0.9 Hz, 1H), 8.63 (d, J = 8.1 Hz, 2H); IR(KBr): 3040, 1691, 1602, 1468, 1445, 801, 758, 727 cm^{-1}; Anal. Calcd for $C_{21}H_{17}BrN_2PtS$: C, 41.73; H, 2.83; N, 4.63; S, 5.31; Br, 13.22%. Found: C, 41.53; H, 3.03; N, 4.52; S, 5.01; Br, 12.95%.

(2,2′-Bipyridine)[2-(4,5-dibromothienyl)](4-methylphenyl)-platinum(II) (7eb): ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.17 (s, 3H), 6.55 (s, 1H), 6.77 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 7.67 (ddd, J = 5.6, 5.7, 1.2 Hz, 1H), 7.78 (ddd, J = 5.6, 5.6, 1.0 Hz, 1H), 8.19 (dd, J = 5.2, 1.2 Hz, 1H), 8.30–8.36 (m, 2H), 8.43 (dd, J = 5.4, 0.8 Hz, 1H), 8.65 (d, J = 8.2 Hz, 2H); IR (KBr): 1483, 1467, 1445, 800, 759, 728 cm^{-1}; Anal. Calcd for $C_{21}H_{16}Br_2N_2PtS$: C, 36.91; H, 2.36; N, 4.10; S, 4.69%. Found: C, 36.15; H, 2.40; N, 3.96; S, 4.83%.

(2,2′-Bipyridine)[2-(5-formylthienyl)](4-methylphenyl)platinum(II) (7ed): ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.16 (s, 3H), 6.76 (d, J = 7.7 Hz, 2H), 6.99 (d, J = 3.7 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 7.68–7.73 (m, 2H), 7.75 (d, J = 3.7 Hz, 1H), 8.20–8.24 (m, 2H), 8.33–8.35 (m, 2H), 8.66 (d, J = 8.0 Hz, 2H), 9.52 (s, 1H); IR(KBr): 1640, 1602, 1397, 1372, 759 cm^{-1}; Anal. Calcd for $C_{22}H_{18}N_2OPtS$: C, 47.74; H, 3.28; N, 5.06; S, 5.79%. Found: C, 47.12; H, 3.29; N, 4.95; S, 5.51%.

(2,2′-Bipyridine)[2-(5-ethoxycarbonylthienyl)](4-methylphenyl)platinum(II) (7ee): ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.23 (t, J = 7.0 Hz, 3H), 2.16 (s, 3H), 4.15 (q, J = 7.0 Hz, 2H), 6.75 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 3.6 Hz, 1H), 7.18 (d, J = 7.7 Hz, 2H), 7.61 (d, J = 3.6 Hz, 1H), 7.66–7.70 (m, 2H), 8.22 (dd, J = 5.5, 0.9 Hz, 1H), 8.27 (dd, J = 5.4, 0.9 Hz, 1H), 8.29–8.30 (m, 2H), 8.63 (d, J = 8.1 Hz, 2H); IR(KBr): 1640, 1602, 1397, 1372, 759 cm^{-1}; Anal. Calcd for $C_{24}H_{22}N_2O_2PtS$: C, 48.24; H, 3.71; N, 4.69; S, 5.37%. Found: C, 48.02; H, 3.95; N, 4.59; S, 4.95%.

(2,2′-Bipyridine)(2-benzothienyl)(4-methylphenyl)platinum(II) (7ef): ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.14 (s, 3H), 6.73 (d, J = 7.4 Hz, 2H), 6.93 (s, 1H), 6.96 (t, J = 7.3 Hz, 1H), 7.10 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.63–7.70 (m, 3H), 8.29–8.35 (m, 3H), 8.38 (dd, J = 5.5, 0.9 Hz, 1H), 8.63–8.66 (m, 2H).

The Reductive Elimination of Arylthiophene 5ea from Aryl(thienyl)platinum Complex 7ea. To a Schlenk tube were

added aryl(thienyl)platinum complex **7ea** (18.1 mg, 0.03 mmol), triphenylphosphine (78.7 mg, 0.3 mmol) and toluene (4 mL). The resulting solution was heated at 95 °C for 1.5 h. After cooling to room temperature, the mixture was washed with water and brine. The organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by column chromatography on silica gel to afford 4.2 mg of 2-bromo-5-(4-methylphenyl)thiophene (**5ea**) in 60% yield. Spectroscopic characteristics and physical properties of the product were identical to the authentic sample.[20]

General Procedure for the Synthesis of Dithienylplatinum(II) Complex. To a mixture of [PtI_2(bpy)] (30.2 mg, 0.05 mmol), 2,3-dibromothiophene (**1b**, 0.027 mL, 0.24 mmol) and potassium fluoride (23.2 mg, 0.4 mmol) in 3 mL of DMSO was added $AgNO_3$ (68.0 mg, 0.4 mmol) in one portion under argon atmosphere. The resulting suspension was stirred at 50 °C for 5 h. After cooling to room temperature, the mixture was passed through a Celite pad, which was washed with dichloromethane repeatedly. The filtrate was washed with water twice. The organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by recrystallization from dichloromethane/hexane to afford 27.8 mg of **8b** as an orange solid (70%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.60 (s, 2H), 7.81 (t, $J = 6.7$ Hz, 2H), 8.33 (d, $J = 4.6$ Hz, 2H), 8.38 (ddd, $J = 7.7$, 7.8, 1.4 Hz, 2H), 8.68 (d, $J = 8.2$ Hz, 2H); IR(KBr): 1598, 1445, 1260, 979, 760, 417 cm^{-1}; Anal. Calcd for $C_{18}H_{10}Br_4N_2PtS_2$: C, 25.95; H, 1.21; Br, 38.36; N, 3.36; S, 7.70%. Found: C, 25.74; H, 1.30; Br, 38.30; N, 3.33; S, 7.47%.

(2,2′-Bipyridine){di[2-(5-bromothienyl)]}platinum(II) (8a): ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.54 (d, $J = 3.5$ Hz, 2H), 6.98 (d, $J = 3.4$ Hz, 2H), 7.77 (ddd, $J = 6.6$, 6.7, 1.0 Hz, 2H), 8.34–8.37 (m, 4H), 8.67 (d, $J = 7.9$ Hz, 2H); IR(KBr): 1601, 1446, 1158, 969, 759, 614, 496, 418; HRMS(FAB) Found: 672.8463, Calcd for $C_{18}H_{12}Br_2N_2PtS_2$: 672.8456.

(2,2′-Bipyridine){di[2-(5-formylthienyl)]}platinum(II) (8d): ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.04 (d, $J = 3.8$ Hz, 2H), 7.75 (ddd, $J = 6.5$, 7.0, 0.6 Hz, 2H), 7.82 (d, $J = 3.7$ Hz, 2H), 8.16 (dd, $J = 4.5$, 1.0 Hz, 2H), 8.38 (ddd, $J = 8.0$, 8.0, 1.0 Hz, 2H), 8.71 (d, $J = 8.5$ Hz, 2H), 9.57 (s, 2H); IR(KBr): 1629, 1508, 1445, 1396, 1367, 1272, 1226, 1049, 816, 760, 740, 658, HRMS(FAB) Found: 574.0290, Calcd for $C_{20}H_{15}N_2O_2PtS_2$ (M + 1): 574.0224.

(2,2′-Bipyridine){di[2-(5-bromo-4-methylthienyl)]}platinum(II) (8g): ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.06 (s, 6H), 6.45 (s, 2H), 7.77 (m, 2H), 8.34–8.39 (m, 4H), 8.65 (d, $J = 8.1$ Hz, 2H); Anal. Calcd for $C_{20}H_{16}Br_2N_2PtS_2$: C, 34.15; H, 2.29; N, 3.98; S, 9.12%. Found: C, 33.54; H, 2.43; N, 4.06; S, 9.08%; HRMS (FAB) Found: 703.8738, Calcd for $C_{20}H_{16}{}^{79}Br^{81}BrN_2S_2{}^{196}Pt$: 703.8743.

Crystal Structure Analysis of 7ee. Single crystals of **7ee**, suitable for X-ray diffraction study were obtained by recrystallization from CH_2Cl_2/hexane. Data for **7ee** were collected on a Rigaku Saturn CCD diffractometer equipped with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Calculations were carried out using the program package Crystal Structure, version 3.7, for Windows. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. **7ee**: $C_{24}H_{22}N_2O_2PtS$, fw: 597.60, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.0772(6)$ Å, $b = 10.0956(5)$ Å, $c = 12.8026(9)$ Å, $\alpha = 66.951(5)°$, $\beta = 73.933(5)°$, $\gamma = 61.988(4)°$, $V = 1051.2(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.888$ g cm^{-3}, No. of unique reflections: 3729 ($I > 3\sigma(I)$), $R = 0.028$, $R_w = 0.036$. Crystallographic data reported in this manuscript have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-682142. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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