Electrophilic Substitution of Platinum(II) Complexes with Thiophene Derivatives

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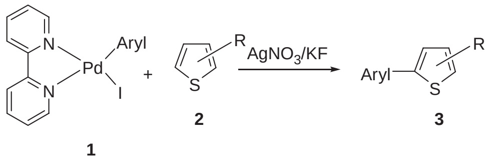
The reaction of aryl(halo)platinum(II)(bpy) complexes with thiophene derivatives causes novel electrophilic substitution in the presence of $AgNO_3/KF$ as an activator to form thienyl complexes in 65–91% yields. The related reaction with (dihalo)-platinum(II) also takes place to afford dithienylplatinum(II) complexes.

Mechanistic studies on a transition-metal-catalyzed reaction with a stoichiometric amount of the metal complex is a powerful tool for the understanding of the reaction pathway involving several fundamental reactions and the actual structure of each key intermediate. We have previously reported that palladium-catalyzed CH arylation and CH homocoupling reactions in the presence of a silver salt as an activator.[1,2] The mechanistic studies have also been performed with a stoichiometric palladium(II) complex and it was found that the reaction of arylpalladium(II) complex **1** with a thiophene derivative **2** afforded the CH arylation product **3** in good yields (eq 1).[3] These findings suggest that the key of the catalytic CH arylation reaction is the electrophilic substitution of arylpalladium(II) complex with thiophene. However, detection of aryl(thienyl)palladium(II) complex has been unsuccessful probably owing to the facile reductive elimination leading to **3**. Accordingly, we envisaged to switch the metal species to platinum, which would retard the reductive elimination step, to afford aryl(thienyl)platinum complex. Herein, we report that aryl(thienyl)platinum complex is obtained by the reaction of the corresponding halide with thiophene derivatives in the presence of a silver salt.



(1)

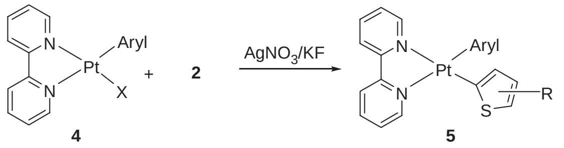
The reaction of the arylplatinum(II) complex **4a**[4] with 2,3-dibromothiophene (**2a**) was first examined with $AgNO_3/KF$ as an activator under similar conditions to those carried out in the reaction of the corresponding palladium complex and found to afford platinum complex **5aa** in 91% yield. ^1H NMR spectrum of the product shows that satellite of ^{195}Pt was observed in the signals of β-H signal of the thiophene [$J(PtH) = 54.6\,Hz$] and ortho-H signal of the aryl moiety [$J(PtH) = 51.6\,Hz$] suggesting that the complex possesses both platinum–aryl and platinum–thienyl bonds (see Supporting Information). It has been completely unsuccessful to detect such arylthienyl complex when the stoichiometric reaction is carried out with the corresponding arylpalladium(II) complex **1**.[3] On the other hand, the obtained platinum(II) complex **5aa** was quite stable in DMSO-d_6 and no reductive elimination was found to occur upon heating at 100 °C for 17 h.

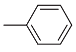
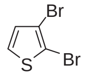
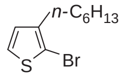
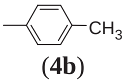
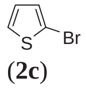
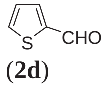
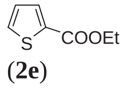
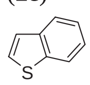
Worthy of note is that this is a new class of reactivity in platinum(II) complexes[5] to allow *intermolecular* electrophilic substitution with a heteroaromatic compound in the presence of $AgNO_3/KF$ without participation of proximal chelation by a heteroatom.[6] It should also be pointed out that the platinum carbon bond formation occurred smoothly at the CH bond when a thiophene derivative bearing a carbon–bromine bond was employed.[7,8]

Table 1 shows that such electrophilic substitution reaction proceeds with several platinum complexes and thiophene derivatives. In addition to platinum(II) iodide complex, it was found that the chloride complex underwent the reaction smoothly to afford the corresponding aryl(thienyl) complex in excellent yields.[9]

Aryl(thienyl)platinum complex **5be** was isolated as single crystals and characterized by X-ray crystallography.[10] Figure 1

Table 1. The reaction of [Pt(Aryl)(X)(bpy)] (**4**) with thiophene derivatives **2**[a]



Aryl	X	Thiophene **2**	Product	Yield/%
 (**4a**)	I	 (**2a**)	**5aa**	91
4a	I	 (**2b**)	**5ab**	87
 (**4b**)	Cl	**2a**	**5ba**	74
4b	Cl	 (**2c**)	**5bc**	65
4b	Cl	 (**2d**)	**5bd**	73
4b	Cl	 (**2e**)	**5be**	74
4b	Cl	 (**2f**)	**5bf**	78

[a] The reaction was carried out with [Pt(Aryl)(X)(bpy)] (**4**) (0.05 mmol) and **2** (0.12 mmol) at 50 °C for 5 h in the presence of $AgNO_3$ (0.2 mmol) and KF (0.2 mmol) in DMSO.

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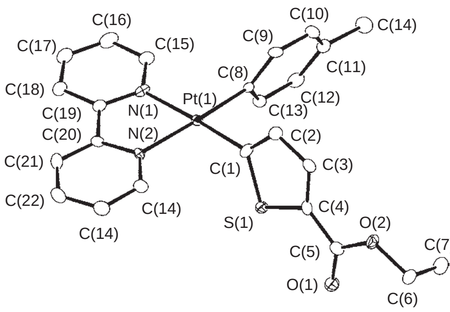
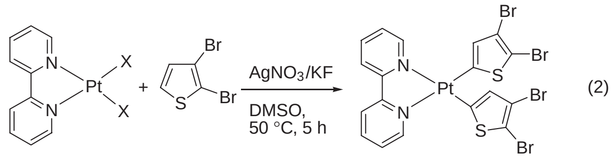


Figure 1. ORTEP drawing of **5be** (50% probability). Hydrogen atoms were omitted for clarity.

depicts the molecular structure of **5be** with a square-planar coordination around the Pt center. The thienyl ligand bonds to platinum center through its α-carbon (Pt(1)–C(1) $= 1.989(6)$ Å).

The reaction of $[Pt(X)_2(bpy)]$ (X = Cl and I) (**6**)[4] was also found to proceed with thiophene through the electrophilic substitution reaction (eq 2).[2] Similarly to the case of the reaction of aryl(halo)platinum complex **5**, chloride and iodide were found to react to afford **7**. The reaction of **6** with 2,3-dibromothiophene (**2a**) in the presence of $AgNO_3$ and KF in DMSO afforded dithienyl complex **7** in 70% yield (X = I) and 65% yield (X = Cl), respectively. The complex **7** is considered to be a platinum analogue for the supposed intermediate of the homocoupling reaction catalyzed by a palladium complex.



6a: X = I
6b: X = Cl
X = I: 70%
X = Cl: 65%
7

In summary, electrophilic substitution of thiophene derivatives with platinum complex to form aryl(thienyl)platinum(II) and dithienylplatinum(II) complexes proceeds by the addition of $AgNO_3$/KF. The results support that the CH substitution reactions of thiophene derivatives proceeds via such an electrophilic substitution reaction. The reactions of platinum complexes **4** and **6** are a class of new reactivity in platinum chemistry to provide a pathway to thienylplatinum(II) complex, where the presence of carbon–halogen bond is tolerable.[11]

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9 The stoichiometric reactions of arylpalladium(II) bromide and chloride were confirmed to proceed similarly to that of iodide.

10 Crystal data for **5be**: $C_{24}H_{22}N_2O_2PtS$: 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, $\alpha = 66.951(5)^\circ$, $\beta = 73.933(5)^\circ$, $\gamma = 61.988(4)^\circ$, $V = 1051.2(1)$ 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 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, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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