Direct formation of arylpalladium(II) complexes from aromatic hydrocarbons via C–H bond activation by the palladium(II) acetate–dipropyl selenide system

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Abstract

Reactions of the palladium(II) acetate–dipropyl selenide system with aromatic hydrocarbons directly affords arylpalladium(II) complexes via aromatic C–H bond activation. In the case of benzene, toluene, *m*-xylene and *p*-xylene, diaryltripalladium(II) complexes $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SePr_2)_2]$ have been obtained. *o*-Xylene and 1,3,5-trimethylbenzene also react with the system, but diaryltripalladium(II) complexes have not been isolated. However, mononuclear arylpalladium(II) complexes [PdArCl(bipy)], derived from all the aromatic compounds cited here, have been obtained after the reactions with the system, followed by treatment with bipy and NaCl. The ability of the palladium(II) acetate–dipropyl selenide system for C–H bond activation of aromatic hydrocarbons has been discussed on the basis of the isolated yields of the resulting arylpalladium(II) complexes.

Introduction

Previously, we have studied the activation of aromatic C–H bonds by the palladium(II) acetate–dialkyl sulfide system [1–3]. In these studies, it was found that benzene and *p*-xylene were directly activated and produced diaryltripalladium(II) complexes $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SR_2)_2]$. Other aromatic compounds such as toluene, *o*-xylene and *m*-xylene did not afford such diaryltripalladium(II) complexes, mainly yielding coupling products, biaryls. However, it was believed that diaryltripalladium(II) complexes were formed in the reaction mixture, because mononuclear arylpalladium(II) complexes [PdArCl(bipy)] were isolated by treatment with bipy and NaCl after the reactions with the system.

The isolation of arylpalladium(II) species by direct activation of aromatic compounds was noteworthy, as these species were considered as key intermediates in the coupling reaction [4, 5], carbonylation [6, 7] and oxidation [8] of aromatic compounds, and also in arylation of olefins [9] by palladium(II) acetate.

In this paper, we report on the formation of arylpalladium(II) complexes directly from aromatic hydrocarbons via C–H bond activation by the palladium(II) acetate–dipropyl selenide system, a selenium analogue of dialkyl sulfide.

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Experimental

All reactions were performed under nitrogen. Solvents were purified by the usual methods. The NMR spectra were measured on a JEOL JNM GX-270 instrument with $CDCl_3$ as solvent. Melting points were determined on a Yanaco melting point apparatus MP-500D. Dipropyl selenide was prepared according to the reported method [10]. ^{1}H NMR ($CDCl_3$): δ 0.99 (t, ^3J(HH) 7.3, $SeCH_2CH_2CH_3$), 1.68 (sex, ^3J(HH) 7.3, $SeCH_2CH_2$), 2.54 (t, ^3J(HH) 7.3, $SeCH_2$).

Preparation of diaryltripalladium(II) complexes $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SePr_2)_2]$ (1–4)

Complexes **1–4** (Scheme 1) were synthesized similarly. A typical example is as follows. A suspension of palladium(II) acetate (0.300 g, 1.34 mmol) and $SePr_2$ (0.147 g, 0.890 mmol) was heated in benzene (20 cm^3) at 90–95 °C for 20 min. Upon cooling, the reaction mixture was filtered and the volatile materials were removed under reduced pressure. The residue was dissolved in ether and diluted with hexane to give 0.074 g of **1** as pale brown microcrystals.

Preparation of mononuclear arylpalladium(II) complexes [PdClAr(bipy)] (5–10)

Complexes **5–10** (Scheme 1) were prepared in a similar way; the preparation of **5** is given as an example.

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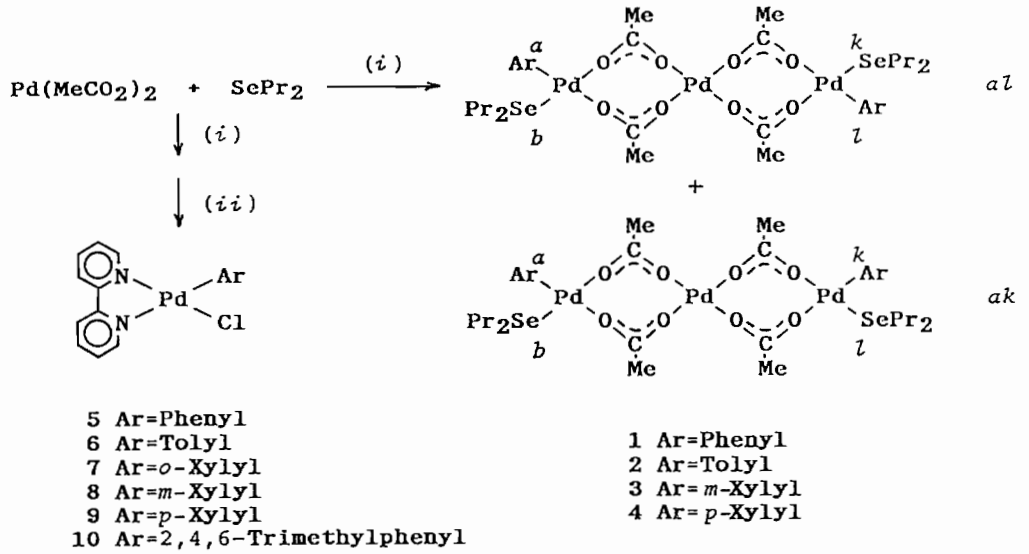

Scheme 1. (i) In ArH at 90–95 °C for 20 min; (ii) bipy followed by NaCl.

A mixture containing palladium(II) acetate (0.100 g, 0.445 mmol) and $SePr_2$ (0.049 g, 0.299 mmol) was heated with benzene (7.5 cm^3) in an oil bath (temperature 90–95 °C) for 20 min. After cooling to ambient temperature, solid bipy (0.070 g, 0.445 mmol) was added and the mixture was stirred for 3 h at room temperature. The resulting mixture was evaporated to dryness, and to the residue acetone (10 cm^3) and then sodium chloride (0.130 g, 2.23 mmol) in water (2 cm^3) were successively added. The mixture was stirred for 12 h at room temperature and then again evaporated to dryness. The residue was extracted with $CHCl_3$ (30 cm^3) to remove the by-product $[PdCl_2(bipy)]$ and was chromatographed on a silica gel column (200 mesh, 18×1.2 cm). The yellow fraction eluted by $CHCl_3$ was collected and was recrystallized from CH_2Cl_2–hexane to give **5** as yellow crystals (0.084 g).

Results and discussion

Benzene, toluene, *m*-xylene and *p*-xylene were directly activated by the palladium(II) acetate–dipropyl selenide system at 90–95 °C for 20 min and produced diaryltripalladium(II) complexes $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SePr_2)_2]$ (Ar = Phenyl (**1**), tolyl (**2**), *m*-xylyl (**3**) and *p*-xylyl (**4**)) (Scheme 1).

Similar diaryltripalladium(II) complexes have been synthesized by the reaction of the palladium(II) acetate–dialkyl sulfide system with benzene [1, 2] or *p*-xylene [3], and were found to be a mixture of two geometrical isomers *al* [(*a*-C_{phenyl}, *b*-$S_{sulfide}$)-(*k*-$S_{sulfide}$, *l*-C_{phenyl})] and *ak* [(*a*-C_{phenyl}, *b*-$S_{sulfide}$)-(*k*-C_{phenyl}, *l*-$S_{sulfide}$)] on the basis of their NMR studies [2]. Complexes **1–4** were also supposed to consist of two geometrical isomers *al* and *ak* (Scheme 1). In the ^1H NMR spectrum of **1** or **4**, acetato methyl protons appeared as four singlets owing to two pairs of equivalent acetato methyl groups in each isomer (Table 1). Signals of the aryl moiety in **1** were observed as two unresolved multiplets centered at δ 6.9(6H) and 7.55(4H), whilst in **4** separated signals due to the two isomers were detected with regard to methyl protons (δ 2.15(3H), 2.17(3H) and 3.03(6H)) and the 6-proton (δ 7.55(1H) and 7.56(1H)).

As for positional isomers of the arylpalladium moiety, aryl groups derived from benzene and *p*-xylene have no isomers, but those derived from toluene and *m*-xylene are supposed to have six and three isomers for each geometrical isomer, e.g. for *al* isomer of **2**, (*a*, *l*) = (2-tolyl, 2-tolyl), (2-tolyl, 3-tolyl), (2-tolyl, 4-tolyl), (3-tolyl, 3-tolyl), (3-tolyl, 4-tolyl) and (4-tolyl, 4-tolyl) are present. Complexes **2** and **3** showed very complicated spectra attributable to overlapping signals owing to both the geometrical and the positional isomers (Table 1). For example, fourteen and ten resonances due to acetato methyl protons were observable for **2** and **3**, respectively.

It is noteworthy that toluene and *m*-xylene were directly activated by the palladium(II) acetate–dipropyl selenide system to produce isolable diaryltripalladium(II) complexes **2** and **3**, though yields were relatively low. Using the palladium(II) acetate–dialkyl sulfide system, such diaryltripalladium(II) species could not be isolated and the yields of arylpalladium(II) complexes [PdArCl(bipy)] obtained by the following reactions with bipy and NaCl were very low (3% for tolyl and 13% for *m*-xylyl) [2, 3].

To ensure the enhanced activity of the palladium(II) acetate–dipropyl selenide system for aromatic C–H bond activation, further investigations described below were performed.

TABLE 1. ^{1}H NMR data[a]

Complex	Dipropyl selenide	Aryl moiety	Acetato-methyl	bipy[b]
1	0.81 (t, ^3J(HH) 7.3, CH_3), 1.00 (t, ^3J(HH) 7.3, CH_3), 1.6 (br, SeCH$_2$CH_2)[c], 1.85 (br, SeCH$_2$CH_2)[c], 2.75 (br, SeCH_2), 2.95(br, SeCH_2)	6.9 (m, C*H*), 7.55 (m, C*H*)	1.78(s), 1.81(s), 1.88(s), 1.91(s)	
2	0.8 (c, CH_3), 1.0 (c, CH_3), 1.4-2.0 (br, SeCH$_2$CH_2)[c], 2.7 (c, SeCH_2), 2.9 (c, SeCH_2), 3.05 (c, SeCH_2)	2.22 (br s, Me), 2.25 (br s, Me), 3.07 (br s, Me), 6.75 (m, C*H*), 7.35 (m, C*H*), 7.75 (m, C*H*)	1.74(s), 1.76(s), 1.79(s), 1.81(s), 1.82(s), 1.83(s) 1.85(s), 1.86(s), 1.87(s), 1.89(s), 1.90(s), 1.91(s) 1.92(s), 1.93(s)	
3	0.81 (br t, ^3J(HH) 7, CH_3), 0.98 (br t, ^3J(HH) 7, CH_3), 1.00 (br t, ^3J(HH) 7, CH_3), 1.4–2.0 (br, SeCH$_2$CH_2)[c], 2.7 (c, SeCH_2), 2.85 (c, SeCH_2), 3.0 (c, SeCH_2)	2.20 (s, Me), 2.22 (s, Me), 3.01 (s, Me), 3.02 (s, Me), 6.55 (m, C*H*), 6.7 (m, C*H*), 7.15 (m, C*H*), 7.6 (m, C*H*)	1.75(s), 1.76(s), 1.81(s) 1.82(s), 1.85(s), 1.87(s), 1.88(s), 1.90(s), 1.91(s), 1.93(s)	
4	0.82 (br t, ^3J(HH) 7.3, CH_3), 0.97 (t, ^3J(HH) 7.3, CH_3), 0.99 (t, ^3J(HH) 7.3, CH_3), 1.4–1.9 (SeCH$_2$CH_2)[c], 1.7 (m, SeCH_2), 1.9 (m, SeCH_2), 3.1 (m, SeCH_2)	2.15 (s, Me), 2.17 (s, Me), 3.03 (s, Me), 6.63 (br d, ^3J(HH) 7, C*H*), 6.75 (d, ^3J (HH) 7.3, C*H*), 7.55 (s, C*H*), 7.56 (s, C*H*)	1.77(s), 1.82(s), 1.88(s), 1.94(s)	
5		6.95–7.15 (m, C*H*), 7.44 (d, ^3J(HH) 7.8, C*H*)		9.30 (d, ^3J(HH) 5.9)
6		2.27 (s, 4-Me)[d], 2.28 (s, 3-Me)[e], 2.71 (s, 2-Me)[f] 6.81 (d, ^3J(HH) 7.3, C*H*)[d], 6.9–7.0 (c, C*H*)[f], 7.22 (d, ^3J(HH) 7.3, C*H*)[d], 7.25–7.45 (c, C*H*)[e,g]		9.3[h]
7		2.21 (s, 3- or 4-Me)[i], 2.22 (s, 3- or 4-Me)[i], 2.25(s, 3-Me)[j], 2.74 (s, 2-Me)[j], 6.75–6.9 (c, 4-~6-H)[j], 6.84 (d, ^3J(HH) 7.8, 5- or 6-H)[i], 7.13 (d, ^3J(HH) 7.8, 5- or 6-H)[i], 7.21 (s, 2-H)[i]		9.2[h]
10		2.26 (s, 4-Me), 2.71 (s, 2- and 6-Me), 6.66 (s, 3- and 5-H)		9.27 (d, ^3J(HH) 5.4)

[a]As for the complexes **8** and **9**, ^{1}H NMR data were already reported in ref. 3. Chemical shifts (δ) in ppm, coupling constants in Hz. Measured in $CDCl_3$ at 30 °C. Key: s = singlet, br = broad, d = doublet, dd = doublet of doublets, t = triplet, and m = multiplet, c = complex. [b]Assigned to 6-H of one pyridyl moiety *trans* to aryl group. Other protons of bipy resonated near at δ 7.3, 7.6, and 7.9–8.1 as complexed pattern. [c]Overlapping with acetato methyl signals. [d]Due to signal of **6c**; see Fig. 1 for the isomers. [e]Due to signal of **6b**. [f]Due to signal of **6a**. [g]Overlapping with bipy signals. [h]Overlapping signals due to isomers. [i]Due to signals of **7b**. [j]Due to signals of **7a**.

TABLE 2. Analytical[a] and physical data for the complexes

Complex	Yield (%)	Melting point[b] (θ (°C))	Analysis (%)		
			C	H	N
1	16	130	37.0(36.8)	4.9(4.8)	
2	15	[c]	37.5(38.2)	5.0(5.1)	
3	18	[c]	39.1(39.3)	5.1(5.3)	
4	50	157	39.5(39.3)	5.1(5.3)	
5	74	205	51.0(51.2)	3.4(3.5)	7.3(7.5)
6	57	[c]	52.7(52.5)	4.1(3.9)	7.1(7.2)
7	41	[c]	52.9(53.6)	4.2(4.3)	6.8(7.0)
8[d]	45	[c]			
9[d]	58	144			
10	13	244	54.4(54.7)	4.5(4.6)	6.5(6.7)

[a]Calculated values in parentheses. [b]With decomposition. [c]Not measured as they consist of isomers. [d]Reported already; see ref. 3.

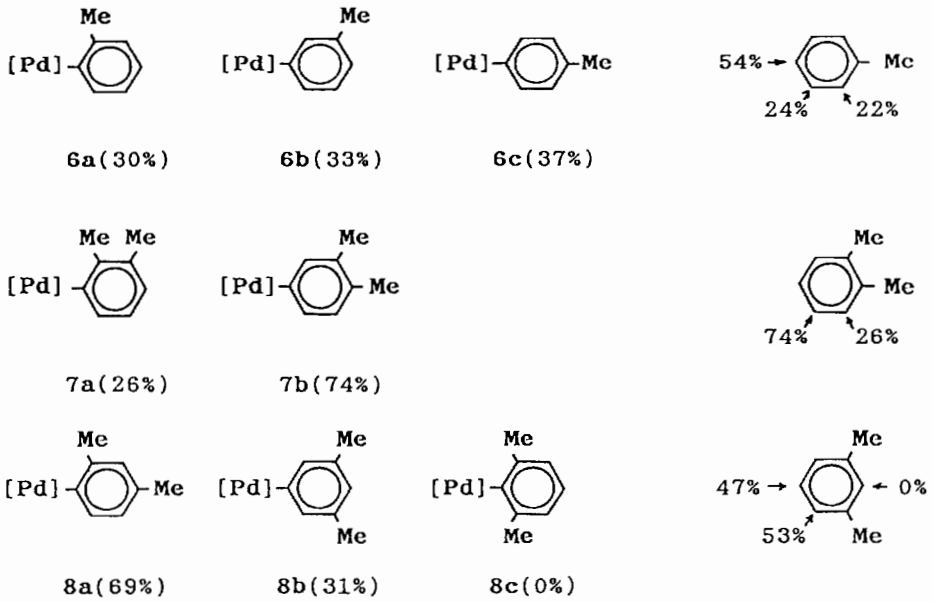

Fig. 1. Isomer distribution of the complexes **6–8** and relative positional reactivities of toluene, *o*-xylene and *m*-xylene. [Pd] denotes PdCl(bipy) moiety.

After the reactions of aromatic compounds with the palladium(II) acetate–dipropyl selenide system at 90–95 °C for 20 min, bipy and then sodium chloride were added to the resulting mixture. In this manner mononuclear arylpalladium(II) complexes [PdArCl(bipy)] (**5–10**, Scheme 1), whose aryl moieties were derived from benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and 1,3,5-trimethylbenzene, were obtained in moderate yields (Table 2). These facts indicated that the palladium(II) acetate–dipropyl selenide system easily activates aromatic C–H bonds and produces the diaryltripalladium(II) species in fairly high yields in the reaction mixture. The lower yields of **1–4** might be associated with their relatively high solubility in common solvents which prevents them from precipitation. The isolation of **7** and **10** strongly supported the above suggestion, as diaryltripalladium(II) complexes derived from *o*-xylene and 1,3,5-trimethylbenzene have not been obtained.

It should be notable that the palladium(II) acetate–dipropyl selenide system activates even the C–H bonds surrounded by two methyl groups in 1,3,5-trimethylbenzene to produce **10**. It was reported that 1,3,5-trimethylbenzene actually did not afford any coupling product or arylpalladium species in a palladium catalyzed coupling reaction [11] or in our palladium(II) acetate–dialkyl sulfide system [3].

Figure 1 shows the isomer distributions of **6–8** and the relative positional reactivities for C–H bond activation of toluene, *o*-xylene and *m*-xylene. The isomer

distributions were determined by the integration values of the methyl ^1H NMR signals in each aryl moiety; methyl protons adjacent to the palladium atom are usually deshielded owing to the magnetic anisotropy of the metal ion having a square planar arrangement [3, 12, 13]. The data of relative positional reactivities suggest that the aromatic C-H bond activation by the palladium(II) acetate-dipropyl selenide system proceeds by an electrophilic substitution mechanism. In the case of m-xylene, though the 5-position has a much lower electron density than the 4- and 6-positions have, relative reactivities were quite close. This phenomenon was ascribed to the difficulty of palladation at the site adjacent to the methyl group due to steric hindrance.

Conclusions

The yields of mononuclear arylpalladium(II) complexes **5-10** were moderate and were much higher than the yields found by the palladium(II) acetate-dialkyl sulfide system (the yields of 6, 7, 8, 9 and **10** were 3%, 11%, 13%, 56% and <1%, respectively) [3]. In particular, it should be noted that even 1,3,5-trimethylbenzene was activated to produce **10 in** 13% yield. In the case of the palladium(R) acetate-dialkyl sulfide system, the main products were coupling products, biaryls, except for benzene and p-xylene. Taking the above facts into consideration, the additive selenide is more effective for C-H bond activation by palladium(II) aeetate and moreover is a better stabilizing ligand for isolation of the generated diaryltripalladium species than the additive sulfide.

The positions to be activated by the palladium(II) acetate-dipropyl selenide system are controlled by a normal electrophilic substitution mechanism, and are influenced by methyl groups due to steric reasons. In conclusion, the palladium(II) acetate–dipropyl selenide system is found to be an excellent reagent for C-H bond activation by palladium(II) acetate.

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