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Facile Oxidative Coupling of Benzene by the Palladium(II) Acetate–Dialkyl Sulfide System

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Synopsis. By the palladium(II) acetate–dialkyl sulfide system, oxidative coupling of benzene has been achieved at 70°C, where palladium(II) acetate alone is inactive for the reaction. Effects of alkyl group on the sulfides, molar ratios of sulfide to palladium(II) acetate, and atmosphere of oxygen have been investigated.

Carbon–hydrogen bond activation is one of the current topics in organometallic chemistry.1) We have been challenging this theme by use of the palladium(II) acetate–dialkyl sulfide system. It has been found that this system activates aromatic C–H bond easily to give unique diaryltripalladium(II) complexes $[\mathrm{Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SR_2)_2}]$ (**1**: Ar=phenyl and *p*-xylyl)2) and the cyclic tetranuclear palladium(II) complexes, $[\mathrm{Pd_4(\mu\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2}]$ (**2**), having dimetallated benzene groups.3)

In the palladium-promoted oxidative coupling,4) alkenylation,5) and carbonylation of aromatic compounds,6) it has been demonstrated that arylpalladium species are generated during the reactions. The above isolated diaryltripalladium(II) complexes (**1**) are regarded as key intermediate for these reactions. Previously, we have reported briefly that biphenyl was formed during the synthetic reactions of diphenyltripalladium(II) complexes.

In this paper, we wish to report the oxidative coupling of benzene by the palladium(II) acetate–dialkyl sulfide system at 70°C where palladium(II) acetate alone is inactive for the reaction.

Results and Discussion

At first it was confirmed that at 70°C oxidative coupling of benzene by palladium(II) acetate alone gave a trace amount of biphenyl.

All the oxidative coupling reactions of benzene described below were carried out in 10 cm^3 of benzene at 70°C for 5 h by the $\mathrm{Pd(O_2CMe)_2}$–$\mathrm{SR_2}$ system, and the yield of biphenyl, based on $\mathrm{Pd(O_2CMe)_2}$, was determined by GLC.

Effects of Sulfides. Oxidative coupling of benzene was investigated with various sulfides, with the $\mathrm{Pd(O_2CMe)_2}$–$\mathrm{SR_2}$ system (2:1 molar ratio). The results are summarized in Table 1. The yields of biphenyl were very low with both $\mathrm{SBu^t_2}$ having bulkier substituents and $\mathrm{SPh_2}$ bearing electron withdrawing substituents, whereas with other sulfides having less bulky and electron donating alkyl substituents, moderate yields were obtained. These results strongly indicate that the coordination of the sulfide ligands to palladium is essential for the C–H bond activation at 70°C. Among the sulfides, $\mathrm{SPr^i_2}$ showed the highest activity.

Table 1. Effect of Sulfide on the Yield of Biphenyl by the $\mathrm{Pd(O_2CMe)_2}$–$\mathrm{SR_2}$ System$^{a)}$

$\mathrm{SR_2}$	Yield (%) of Ph-Ph$^{b)}$ under $\mathrm{N_2}$	Yield (%) of Ph-Ph$^{b)}$ under $\mathrm{O_2}$
$\mathrm{SBu^t{}_2}$	5	9
$\mathrm{SPr^i{}_2}$	49	66
$\mathrm{SBu^i{}_2}$	33	48
$\mathrm{SPr_2}$	31	48
$\mathrm{SEt_2}$	34	49
$\mathrm{SPh_2}$	4	4

a) Reaction conditions: $\mathrm{Pd(O_2CMe)_2}$, 0.223 mmol; $\mathrm{SR_2}$, 0.111 mmol; benzene, 10 cm^3; at 70°C for 5 h. b) Determined by GLC analysis. Based on $\mathrm{Pd(O_2CMe)_2}$.

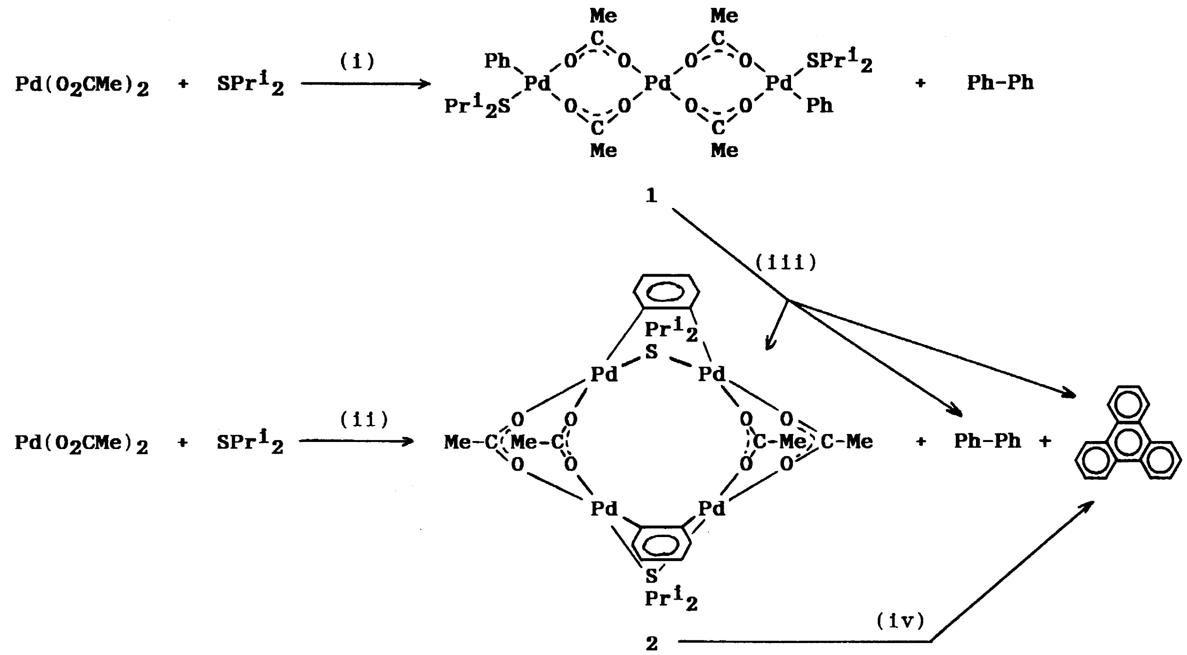
Effect of the Molar Ratio of $\mathbf{SR_2}$: $\mathbf{Pd(O_2CMe)_2}$. As summarized in Table 2, using $\mathrm{SPr^i_2}$ as the most promising one, effect of the molar ratio of $\mathrm{SPr^i_2}$: $\mathrm{Pd(O_2CMe)_2}$ was investigated. Lower yield of biphenyl was obtained when the molar ratio was 2:1, indicating that excess sulfide blocks the coordination sites for benzene molecule to interact with palladium. On the contrary, even with a small amount of sulfide (1:8 ratio), a moderate yield was obtained. This result suggests that the sulfide ligands, liberated by the decomposition of the initially formed diphenyltripalladium(II) complex (**1**), are coordinated again to the unreacted palladium(II) acetate, and then the species having sulfide ligands forms the complex (**1**). Among the several molar ratios, the ratio of 1:2 gave the best yield.

As for the reactive species for the formation of the

Table 2. Effect of Molar Ratio of $\mathrm{SR_2}$: $\mathrm{Pd(O_2CMe)_2}$ on the Yield of Biphenyl by the $\mathrm{Pd(O_2CMe)_2}$–$\mathrm{SPr^i_2}$ System$^{a)}$

Molar ratio of $\mathrm{SPr^i{}_2}$: $\mathrm{Pd\ (O_2CMe)_2}$	Yield (%) of Ph-Ph$^{b)}$
2 : 1	25
1 : 1	45
2 : 3	41
1 : 2	49
1 : 4	45
1 : 8	32

a) Reaction conditions: $\mathrm{Pd(O_2CMe)_2}$, 0.223 mmol; benzene 10 cm^3; at 70°C for 5 h under nitrogen atmosphere. b) Determined by GLC analysis. Based on $\mathrm{Pd(O_2CMe)_2}$.



Scheme 1. Preparation and reactions of the diaryltripalladium(II) complex **1** (Ar=Ph, $SR_2=SPr^i_2$) and the cyclic tetranuclear palladium(II) complex **2** ($SR_2=SPr^i_2$). (i) Benzene, 70°C, 30 min. (ii) Benzene, 90°C, 1 h. (iii) Benzene, 90°C, 1 h. (iv) Benzene, 90°C, 21 h.

complex (**1**), three species containing sulfide ligands, i.e. $[Pd(O_2CMe)_2(SR_2)_2]$, $[Pd_2(\mu\text{-}O_2CMe)_2(O_2CMe)_2(SR_2)_2]$, and $[Pd_3(\mu\text{-}O_2CMe)_4(O_2CMe)_2(SR_2)_2]$, are possible. We have found that the first mononuclear complex produced the complex (**1**),[2] but it is not clear whether the second dinuclear and the third trinuclear complexes could afford the complex (**1**).

Effect of Oxygen. As shown in Table 1, the oxidative coupling reactions performed under oxygen atmosphere gave higher yields of biphenyl as compared with those carried out under nitrogen atmosphere. Moreover, after 1 day the reaction by the $Pd(O_2CMe)_2$– SPr^i_2 system (molar ratio of $SPr^i_2 : Pd(O_2CMe)_2 = 1:2$) under oxygen atmosphere afforded biphenyl and triphenylene in 116 and 29% yields (based on $Pd(O_2CMe)_2$), respectively.

Previously, we have reported that the reaction of the $Pd(O_2CMe)_2$–SPr^i_2 system with benzene at 70°C afforded the diphenyltripalladium(II) complex (**1**) and biphenyl, whereas the same reaction carried out at 90°C yielded the cyclic tetranuclear palladium(II) complex (**2**), biphenyl and triphenylene.[2,3] It has been also found that the tetranuclear complex (**2**) was decomposed in refluxing benzene to give triphenylene in 22% yield and moreover the trinuclear complex (**1**) was converted into the tetranuclear complex (**2**) with the formation of biphenyl and triphenylene[3] (Scheme 1). These facts clearly showed that initially the system reacted with benzene to afford the diphenyltripalladium(II) complex (**1**), followed by the formation of biphenyl and the tetranuclear complex (**2**), and that by the prolonged heating tripheylene was produced by the decomposition of the complex (**2**).

Considering that 1 mole of $Pd(O_2CMe)_2$ affords 1/3 mole of the trinuclear complex (**1**) and **1** is decomposed to give 1/3 mole of biphenyl, the theoretical yield of biphenyl is calculated at 33% based on $Pd(O_2CMe)_2$. However, accompanying the decomposition of 1/3 mole of **1**, it is supposed that 1/3 mole of $Pd(O_2CMe)_2$ is released and this liberated 1/3 mole of $Pd(O_2CMe)_2$ could form 1/9 mole of **1**. If this process continues endlessly, the maximum yield of biphenyl can be calculated at 50% based on $Pd(O_2CMe)_2$ [geometric series $\sum_{1}^{\infty}(1/3)^r=0.5$]. As described above, in the reaction for 1 day under oxygen atmosphere the yield of biphenyl was 116% based on $Pd(O_2CMe)_2$, indicating that the oxidative coupling proceeds catalytically.

In conclusion, it was found that the $Pd(OCMe)_2$–SR_2 system activates the C–H bonds of benzene under milder conditions (70°C) as compared with $Pd(O_2CMe)_2$ alone to give the coupling product biphenyl. However, even by the system, mesitylene did not afford any coupling products at 70°C.

Experimental

Materials. Palladium(II) acetate was prepared according to the procedure of Wilkinson and co-workers.[7] Benzene was dried over calcium hydride and distilled, and degassed by the stream of nitrogen or oxygen before use.

General Procedure for the Oxidative Coupling of Benzene by the $Pd(O_2CMe)_2$–SR_2 System. Typical reaction conditions were shown below. In a two-necked flask, palladium(II) acetate (0.050 g, 0.223 mmol), diisopropyl sulfide (0.013 mg, 0.111 mmol), and benzene (10 cm^3) were placed under nitrogen or oxygen atmosphere. The resulting mixture was heated at 70°C under nitrogen or oxygen atmosphere for appropriate reaction times. Analysis of the products was carried out on a Shimadzu GC-14A gas chromatograph with a flame ionization detector on a BP-1 (50 m×0.25 mm) capillary column. Biphenyl and triphenylene were identified by comparison of GLC retention times with authentic samples. Yields of biphenyl and triphenylene based on palladium(II) acetate were determined using hexadecane as an internal standard. Yields were averaged values of three experiments.

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