

Mechanism of Reaction of *trans*-Bis(diethylphenylphosphine)di-*m*-tolylpalladium(II) with Methyl Iodide Affording *m*-Xylene. Evidence for a Reductive Elimination Process Involving Intermolecular Exchange of Organic Groups

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Received March 4, 1986

Reaction of *trans*-PdAr₂L₂ (1, Ar = *m*-tolyl, L = PEt₂Ph) with MeI in benzene yielded *m*-xylene over 70% selectivity together with 3,3'-bitolyl. Addition of *trans*-PdMe(I)L₂ (2) to the system significantly enhanced the reaction rate and the selectivity for *m*-xylene formation. Kinetic and deuterium-labeling studies have indicated that formation of *m*-xylene proceeds through an intermolecular process between 1 and 2, the latter of which is formed by oxidative addition of MeI to the Pd⁰-PEt₂Ph species generated in the reaction.

Introduction

There is current interest in reductive elimination reaction of d⁸ diorgano-transition-metal complexes in connection with various transition-metal-catalyzed organic reactions.^{1,2} Reductive elimination reaction is frequently accelerated by action of organic halides.² Such a process is assumed as an important step in nickel- and palladium-catalyzed cross-coupling reactions of organic halides and organomagnesium halides.³ For palladium alkyls, Stille et al. have shown that reductive elimination of ethane from *cis*- and *trans*-PdMe₂L₂ (L = tertiary phosphine ligand) are markedly enhanced by addition of MeI.^{2a,b} For these reactions they have proposed mechanisms involving trimethylpalladium(IV) iodide intermediates. Similar mechanisms involving triorgano-palladium(IV) intermediates are currently assumed for reactions of diorgano-palladium(II) complexes with organic halides.^{2a-f}

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(3) (a) Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kogotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* 1982, 104, 108. (b) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *Ibid.* 1984, 106, 158. (c) Sekiya, A.; Ishikawa, N. *J. Organomet. Chem.* 1977, 125, 281; 1976, 118, 349. (d) Minato, A.; Tamao, K.; Hayashi, T.; Suzuki, K.; Kumada, M. *Tetrahedron Lett.* 1981, 22, 5319; 1980, 21, 845. (e) Corriu, R. J.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* 1972, 144. (f) Tamao, K.; Sumitani, K.; Kiso, Y.; Zenbayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* 1976, 49, 1958 and references therein.

Table I. Effect of Addition of *trans*-PdMe(I)L₂ (2) on the Rates of *m*-Xylene Formation in the Reactions of *trans*-PdAr₂L₂ (1) and MeI in Benzene at 50 °C^a

[2] _{ad} , M	10 ⁴ k _{obsd} , s ⁻¹
0.05	1.8
0.10	2.5
0.20	3.6
0.30	3.7
0.50	4.1

^a Initial concentration: [1] = 0.10 M; [MeI] = 2.0 M.

In this paper we report our new findings on the reaction of *trans*-PdAr₂L₂ (1, Ar = *m*-tolyl, L = PEt₂Ph) with MeI to give *m*-xylene. Kinetic and deuterium-labeling studies indicate that the *m*-xylene formation proceeds not through the mechanism involving a Pd(IV) intermediate but through a novel reaction process involving an intermolecular reaction between 1 and *trans*-PdMe(I)L₂ (2), which is formed by oxidative addition of MeI to Pd⁰-PEt₂Ph species generated in the reaction.

Results

Reaction of *trans*-PdAr₂L₂ (1) with MeI. Treatment of *trans*-ditolylpalladium complex (1, 0.1 M) with MeI (20 equiv/1) in benzene at 50 °C for 5 h yielded 75% / 1 of *m*-xylene and 25% of 3,3'-bitolyl. The reaction afforded also *trans*-methylpalladium iodide (2) and *trans*-PdAr(I)L₂ (3), the amounts of which corresponded to those of 3,3'-bitolyl and *m*-xylene, respectively.

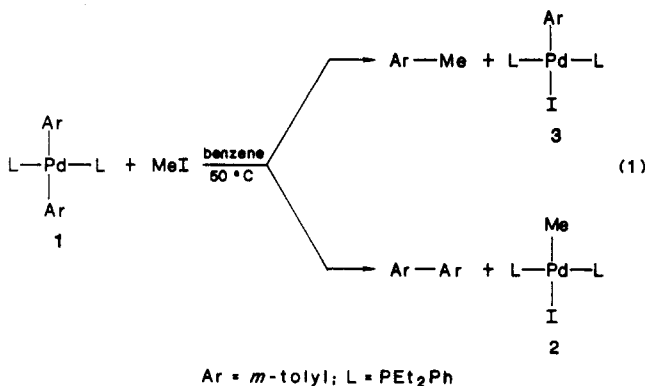


Figure 1 (a and a') shows time courses of *m*-xylene and 3,3'-bitolyl formation in reaction 1, which was followed by

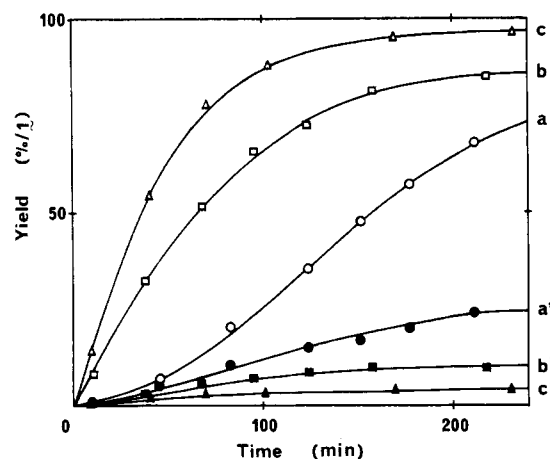


Figure 1. Time-yield curves for formation of *m*-xylene and 3,3'-bitolyl in the reactions of *trans*-PdAr₂L₂ (1; 0.1 M) and MeI (2.0 M) in benzene at 50 °C in the absence and presence of added *trans*-PdMe(I)L₂ (2). Curves a, b, and c are for *m*-xylene formation and curves a', b', and c' for 3,3'-bitolyl formation. Initial amount of added 2 (M): 0.00 (a, a'), 0.05 (b, b'), 0.30 (c, c').

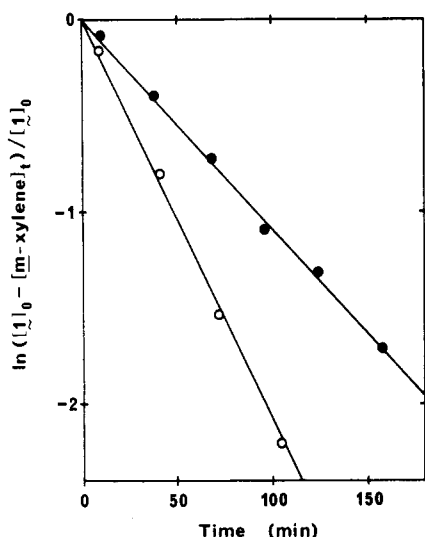


Figure 2. Typical first-order plots for *m*-xylene formation in the reactions of *trans*-PdAr₂L₂ (1; 0.10 M) and MeI (2.0 M) in benzene at 50 °C in the presence of added *trans*-PdMe(I)L₂ (2). Concentration of added 2 (M): 0.05 (●), 0.30 (○).

means of HPLC as well as ³¹P{¹H} NMR spectroscopy. In the ³¹P{¹H} NMR spectrum of a benzene solution of 1 and MeI, the signal due to 1 decreased with an increase of signals due to 2 and 3 as the reaction progressed. No signal other than those of 1–3 was detected throughout the reaction. The time-yield curves for formation of 2 and 3 were similar to those for 3,3'-bitolyl and *m*-xylene, respectively.

The S-shaped time-yield curves a and a' in Figure 1 suggest the occurrence of an autocatalytic process. Addition of 2 to the system significantly enhances the reaction rate and the selectivity for *m*-xylene formation (b and c). Furthermore, a marked change is observed in the shape of the time-yield curve for the *m*-xylene formation. Thus, in the presence of over 0.5 equiv of added 2, the S-shaped curves are not observed and the *m*-xylene formation obeys approximate first-order kinetics in the concentration of 1 (Figure 2). Table I shows dependence of the first-order rate constants for *m*-xylene formation (*k*_{obsd}) on the concentration of added 2 ([2]_{ad}). Plot of reciprocals of *k*_{obsd} and [2]_{ad} gave a straight line (Figure 3). In the presence of three times excess amount of added 2 to 1, *k*_{obsd} values were constant regardless of the concentration of MeI in

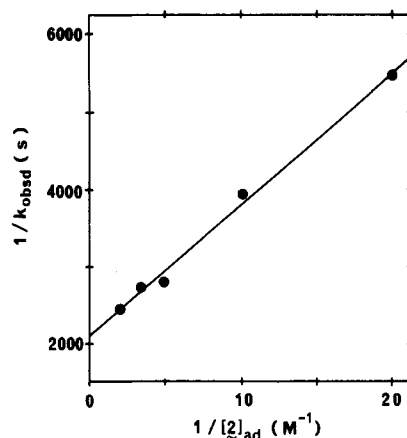
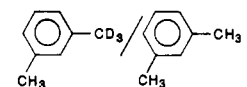


Figure 3. Plot of 1/*k*_{obsd} vs. 1/[2]_{ad}.

Table II. Effect of Addition of *trans*-Pd(CH₃)(I)L₂ (2-*d*₀) on the Ratio of Nondeuterio- to Trideuterio-*m*-xylene Produced in the Reactions of *trans*-Pd(*m*-CH₃C₆H₄)₂L₂ (1) and CD₃I in Benzene at 50 °C^a

amount of added 2- <i>d</i> ₀ , mol/mol of 1		
	found	calcd ^b
0.0	100/0	100/0
1.0	35/65	37/63
2.0	20/80	21/79
3.0	16/84	15/85
5.0	11/89	9/91

^a Values at 100% conversion of 1. ^b See text.

the concentration range of 1.0–2.0 M (10⁴*k*_{obsd} = 3.6 ± 0.1 s⁻¹). The reaction was effectively retarded by addition of free PET₂Ph to the system. Accurate magnitude of the retardation effect of free PET₂Ph, however, could not be determined because MeI reacted with free PET₂Ph to form phosphonium iodide salt.

Deuterium-Labeling Study. *m*-Xylene liberated in the reaction of nondeuterio complex 1 with CD₃I (isotopic purity, 99%) in the absence and presence of *trans*-PdCH₃(I)L₂ (2-*d*₀) was examined by mass spectrometry. The results are listed in Table II. In the absence of 2-*d*₀ the reaction gives trideuterio-*m*-xylene, selectively. On the other hand, in the presence of 2-*d*₀ the reaction affords nondeuterio- as well as trideuterio-*m*-xylenes. Relative ratio of nondeuterio- to trideuterio-*m*-xylene increases with increasing amount of 2-*d*₀.

Reaction of *trans*-PdAr₂L₂ (1) with *trans*-PdMe(I)L₂ (2) in the Absence of MeI. The results described above strongly suggest that *m*-xylene is formed by the reaction of 1 with 2 not by the direct reaction of 1 with MeI. Thus, we next examined the reaction of 1 and 2 in the absence of MeI.

The reaction of 1 and 2 in a 1:1 ratio in benzene containing dimethyl maleate (dmm) at 60 °C was followed by means of HPLC and ³¹P{¹H} NMR spectroscopy. In this experiment, addition of dmm to the system was essential to achieve the clean reaction of 1 and 2. In the absence of dmm, thermolysis of 1 affording 3,3'-bitolyl proceeded rapidly. Further study on the thermolysis indicated that the bitolyl formation was induced by the coordinatively unsaturated [Pd(PET₂Ph)₂] species, which was effectively trapped as Pd-olefin complexes by addition of dmm to the system (see Experimental Section).

Figure 4 shows the time course of the reaction of 1 and 2 as followed by means of HPLC. Up to 40% conversion

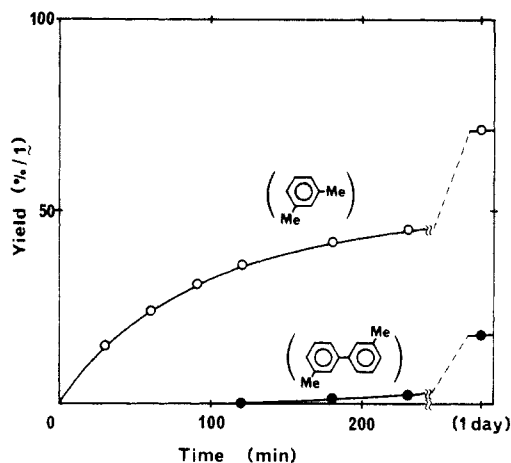
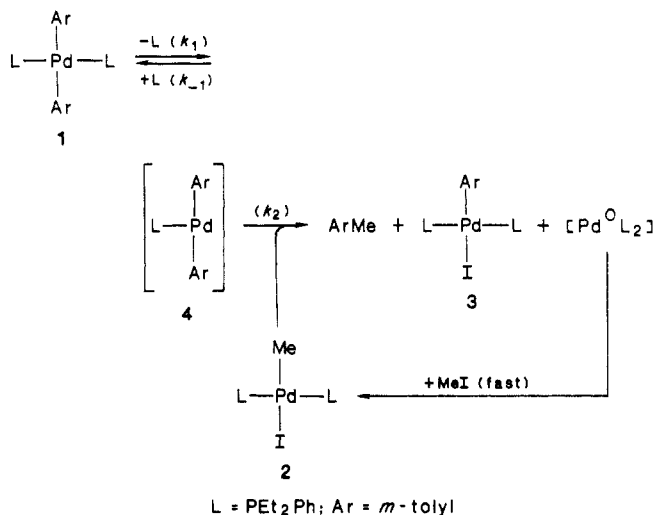


Figure 4. Time-yield curves for formation of *m*-xylene and 3,3'-bitolyl in the reaction of *trans*-PdAr₂L₂ (1; 0.1 M) and *trans*-PdMe(I)L₂ (2; 0.1 M) at 60 °C in benzene containing dimethyl maleate (0.2 M).

Scheme I



of 1, the reaction selectively gives *m*-xylene together with *trans*-PdAr(I)L₂ (3) and Pd(0)-olefin complexes Pd(olefin-*trans*-PdAr₂L + *trans*-PdMe(I)L $\xrightarrow[\text{benzene}]{\text{dmm}}$ Ar-Me + *trans*-PdAr(I)L + Pd(olefin)L₂ (2) 3

Ar = *m*-tolyl; L = PEt₂Ph; olefin = dimethyl maleate or dimethyl fumarate (fin)L₂ (olefin = dmm or dimethyl fumarate (dmf)).⁴ On further reaction the system formed a minor amount of 3,3'-bitolyl in addition to *m*-xylene.⁵ Reaction 2 was completely blocked by addition of PEt₂Ph (2 equiv/1) to the system.

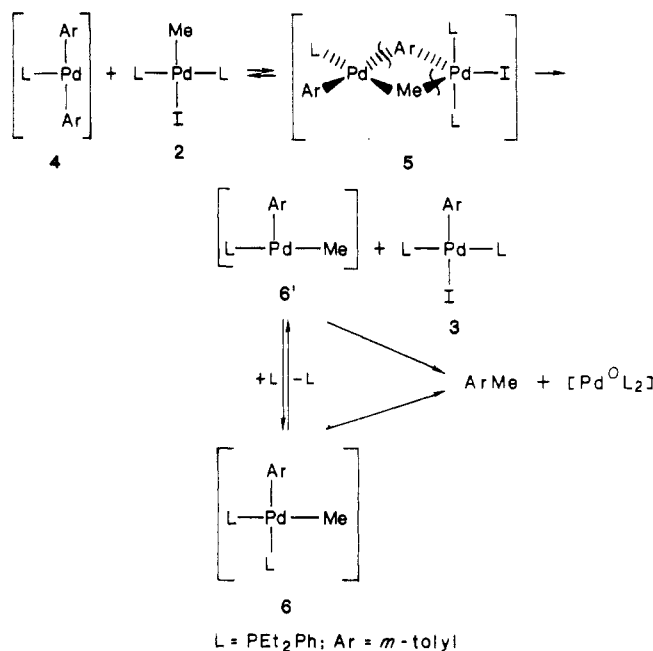
Discussion

The present results indicate that the major part of the *m*-xylene formation in reaction 1 proceeds through an intermolecular reaction process between 1 and 2. As the most likely process we propose the reaction mechanism illustrated in Scheme I. Dissociation of the PEt₂Ph ligand

(4) Since *cis*-*trans* isomerization of dmm is catalyzed by the Pd⁰-PEt₂Ph species and PEt₂Ph in the system, the olefin-coordinated Pd(0) species were obtained as a mixture of complexes coordinated with both dmm and dmf.

(5) Since addition of dmm was found to retard reaction 2, direct comparison of reaction rates between reactions 1 and 2 could not be made (see Experimental Section).

Scheme II



(L) from 1 gives a T-shaped three-coordinate ditolyl intermediate (4). Reaction of 4 and 2 yields *m*-xylene (ArMe) together with 3 and the Pd⁰-PEt₂Ph species, the latter undergoing rapid oxidative addition of MeI to reproduce 2.

Assumption of the steady-state approximation for the concentration of 4 in Scheme I leads to the following kinetic equation.

$$\frac{d[\text{ArMe}]}{dt} = \frac{k_1 k_2 [2][1]}{k_{-1}[L] + k_2[2]} \quad (3)$$

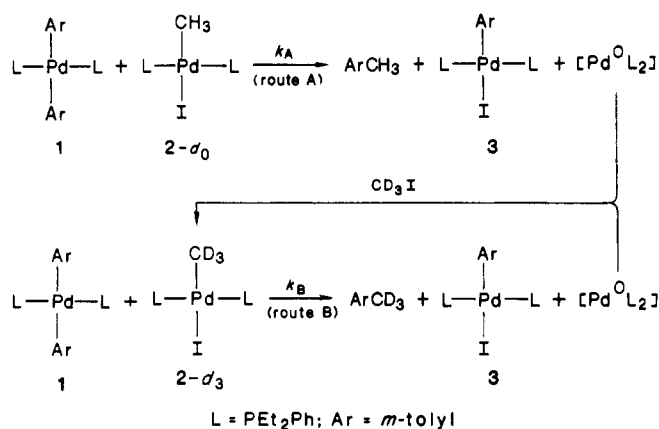
In the presence of added 2, reaction 1 formed *m*-xylene and monotolyl complex 3 over 90% selectivity. Thus, the side reaction affording 3,3'-bitolyl and monomethyl complex 2 can be ignored, and 2 is maintained almost at the initial concentration throughout the reaction. Under such a situation *m*-xylene formation obeys first-order kinetics in the concentration of 1, and *k*_{obsd} can be expressed by the following equation, in which 1/*k*_{obsd} is proportional to the reciprocal of [2]_{ad} in agreement with the experimental result shown in Figure 3.

$$\frac{1}{k_{\text{obsd}}} = \frac{k_{-1}[L]}{k_1 k_2 [2]_{\text{ad}}} + \frac{1}{k_1} \quad (4)$$

For the intermolecular reaction of 4 and 2 in Scheme I, we postulate the mechanism shown in Scheme II. Intermolecular exchange of methyl and *m*-tolyl groups through intermediate 5 will give three-coordinate *cis*-methyl-*m*-tolylpalladium complex 6' and 3.⁶ Reductive

(6) Similar intermolecular exchange processes of anionic ligands through dinuclear intermediates bridged by two anionic ligands have been proposed for the disproportionation and isomerization reactions of d⁸ square-planar complexes: (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1981, 43, 1868. (b) Ozawa, F.; Kurihara, K.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* 1985, 279, 233. (c) Scott, J. D.; Puddephatt, R. J. *Organometallics* 1983, 2, 1643 and references cited therein. (d) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* 1980, 9, 185. (e) Garrou, P. E. *Adv. Organomet. Chem.* 1984, 23, 95. (f) Venanzi, L. M. *Coord. Chem. Rev.* 1982, 43, 251. (g) Bachechi, F.; Bracher, G.; Grove, D. M.; Kellenberger, B.; Pregosin, P. S.; Venanzi, L. M.; Kellenberger, B.; Pregosin, P. S.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* 1983, 22, 1031. (h) Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F. *Ibid.* 1983, 22, 2324. (i) Tulip, T. H.; Yamagata, T.; Yoshida, T.; Wilson, R. D.; Ibers, J. A.; Otsuka, S. *Ibid.* 1979, 18, 2239. (j) Paonessa, R. S.; Troglor, W. C. *Ibid.* 1983, 22, 1038.

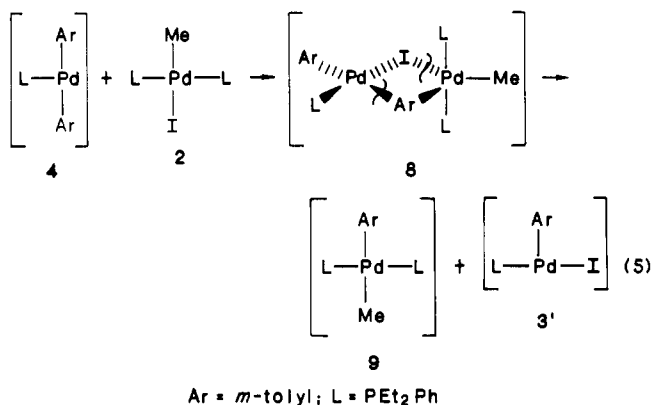
Scheme III



elimination of *m*-xylene directly from 6' or after coordination of L to afford 6 gives the Pd⁰-PEt₂Ph species, which rapidly undergoes oxidative addition of MeI to yield 2.

Intermediacy of *cis*-methyl-*m*-tolylpalladium complexes 6 and 6' has been supported by examination of thermolysis behavior of isolated *cis*-Pd(CH₃)(Ph)(PEt₂Ph)₂ (7), the complex analogous to 6.⁷ Complex 7 has been found to readily decompose in benzene even at room temperature to give an almost quantitative amount of toluene. Furthermore, thermolysis of 7 in benzene containing 20 equiv of CD₃I afforded CH₃Ph in 97% selectivity together with a minor amount of CD₃Ph.

Another possible reaction mechanism between 4 and 2 is the one involving a dinuclear intermediate (8), in which two palladium centers are bridged by iodo and *m*-tolyl ligands. In this case exchange of iodo and *m*-tolyl ligands



gives the *trans*-methyl-*m*-tolyl complex 9 and the monomethyl complex 3'. However, *trans*-Pd(Ph)Me(PEt₂Ph)₂ complex, which was separately prepared as a model of 9, proved to be thermally stable and gave predominantly ethane on reaction with MeI.⁸ Thus, involvement of a process as represented by eq 5 is unlikely.

On the basis of these results and considerations we now examine the results of the deuterium-labeling experiment. The processes for formation of trideuterio- and non-deuterio-*m*-xylenes can be expressed by Scheme III. The reaction of 1 and *trans*-PdCH₃(I)L₂ (2-*d*₀) gives non-deuterio-*m*-xylene (ArCH₃) together with 3 and Pd(0) species, which reacts with CD₃I to give *trans*-PdCD₃(I)-(PEt₂Ph)₂ (2-*d*₃) (route A). The reaction of 2-*d*₃ with 1

affords trideuterio-*m*-xylene (ArCD₃) together with 3 and the Pd(0) species, the latter further reproducing 2-*d*₃ on interaction with CD₃I.

If complexes 2-*d*₀ and 2-*d*₃ have the same reactivity toward 1 (*k*_A and *k*_B), the ratio of trideuterio- to non-deuterio-*m*-xylene produced can be estimated as listed in Table II (see Appendix for calculation). The calculated values are in agreement with the experimental values within experimental error.

The side reaction in reaction 1 yielding 3,3'-bitolyl and monomethyl complex 2 was found to proceed through a similar intermolecular process between 1 and 3. This is the reason for formation of bitolyl at the later stage of reaction 2 observed in Figure 4. The results will be reported elsewhere.

Finally, we must consider the initial inductive stage of reaction 1, where complexes 2 and 3 are not present. The following processes are possible as the initiation step: (i) thermal decomposition of 1 and succeeding oxidative addition of MeI to the resulted Pd(0) species, (ii) MeI may interact with 1 by an unidentified process such as a charge-transfer reaction and induce reductive elimination of 3,3'-bitolyl from 1 without involving Pd(IV) intermediate, the process being followed by oxidative addition of MeI to Pd(0) species, and (iii) oxidative addition of MeI to 1 giving ditolylmethylpalladium(IV) intermediate and reductive elimination of 3,3'-bitolyl or *m*-xylene from the Pd(IV) species. Among these processes (i) can be excluded because in the absence of MeI complex 1 is fairly stable in solution even at 60 °C, while it may be difficult to get experimental evidence to prove or disprove processes ii or iii.

Although the above-mentioned uncertainty still remains regarding the initial stage of the reaction, the experimental evidence provided here strongly indicates that the reaction of the diarylpalladium(II) with methyl iodide does not require the involvement of a palladium(IV) intermediate once the methylpalladium(II) iodide is formed in the system. However, the present results should not be construed to exclude the possibility of involvement of a Pd(IV) intermediate in any reaction systems between diorganopalladium(II) complexes and organic halides. In fact our own examination of the reactions of *cis*-dimethylbis(tertiary phosphine)palladium complexes with methyl iodide confirmed previous results of Stille,^{2a} who suggested the participation of trimethylpalladium(IV) iodide as an intermediate. On the other hand, we have confirmed that the reaction of *cis*-PdPh(CH₃)(PEt₂Ph)₂ with CD₃I gave PhCH₃ in 97% selectivity, a result compatible with an intramolecular reductive elimination process without involvement of a Pd(IV) species.⁷ These lines of evidence seems to indicate that the reaction course between a diorganopalladium(II) complex and an organic halide may vary depending on the nature of the diorganopalladium(II) complex and possibly on the organic halide.

Experimental Section

All manipulations were carried out under an atmosphere of nitrogen or argon or in vacuo. Infrared spectra were recorded on a Hitachi 295 spectrometer. ¹H and ³¹P{¹H} NMR spectra were measured on a JEOL FX-100 spectrometer. ¹H and ³¹P NMR signals are referred to Me₄Si as an internal standard and PPh₃ as an external standard, respectively. Elemental analyses were carried out by Mr. T. Saito and Dr. M. Tanaka of our laboratory using Yanagimoto CHN Autocorder type MT-2 and Yawata Halogen Analyzer. Organic compounds formed by the reactions were analyzed by HPLC (Shimadzu LC-4A, RI detector, Zorbax ODS column, MeOH-H₂O (4:1)). Mass spectra were measured on a Hitachi M-80 GC-MS spectrometer.

Preparation of *trans*-Pd(*m*-tolyl)₂(PEt₂Ph)₂ (1). To a

(7) Ozawa, F.; Toyoshima, T.; Yamamoto, T.; Yamamoto, A., unpublished results.

(8) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A., unpublished results: the reaction of *trans*-Pd(Ph)Me(PEt₂Ph)₂ with MeI in Ph₂O at 45 °C gave 59% Pd of ethane and 33% of PhMe.

heterogeneous yellow mixture of $\text{PdBr}_2(\text{PEt}_2\text{Ph})_2$ (2.5 g, 4.1 mmol) and Et_2O (20 mL) containing styrene (75 μL , 0.7 mmol)⁹ was added an Et_2O solution (13 mL) of *m*-tolyllithium (10 mmol) at -70°C stirred magnetically for 30 min. On addition of *m*-tolyllithium, color of the system gradually turned to pale yellow. The reaction mixture was stirred for 2 h at -30°C . The resulted white precipitate was filtered, washed with hexane (10 mL \times 3) at -70°C , and dried in vacuo at 0°C . The crude product was recrystallized from acetone- CH_2Cl_2 to yield white crystals of **1** (1.7 g, 68%): dec in vacuo, 82°C ; ^1H NMR (CD_2Cl_2 , -20°C) δ 0.84 (quintet, $J = 7.7$ Hz, 12 H, PCH_2CH_3), 1.27–1.52 (m, 8 H, PCH_2CH_3), 2.10 (s, 6 H, CH_3 in *m*-tolyl); $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2 , -20°C) 20.1 (s). Anal. Calcd for $\text{C}_{34}\text{H}_{44}\text{P}_2\text{Pd}$: C, 65.8; H, 7.1. Found: C, 65.8; H, 7.1.

Preparation of *trans*-PdMe(I)(PEt₂Ph)₂ (2). To a heterogeneous white mixture of *trans*- $\text{PdMe}_2(\text{PEt}_2\text{Ph})_2$ ^{8a,10} and acetone (7 mL) was added an aqueous HI solution (0.80 mmol, 103 μL) at -30°C . The system turned to a pale yellow homogeneous solution on stirring at room temperature. After 2 h dichloromethane (5 mL) was added to the system. The organic layer was separated, dried over MgSO_4 , and concentrated to dryness to give a pale yellow solid, which was recrystallized from acetone to give crystals of **2** (0.35 g, 76%): ^1H NMR (CD_2Cl_2 , room temperature) δ 0.19 (t, $J = 6.1$ Hz, 3 H, PdCH_3), 1.08 (quintet, $J = 7.6$ Hz, 12 H, PCH_2CH_3), 2.14–2.40 (m, 8 H, PCH_2CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , room temperature) 24.8 (s). Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{IP}_2\text{Pd}$: C, 43.4; H, 5.7; I, 21.9. Found: C, 43.5; H, 5.9; I, 22.0.

Preparation of *trans*-Pd(*m*-tolyl)I(PEt₂Ph)₂ (3). To a heterogeneous white mixture of **1** (0.30 g, 0.49 mmol) and acetone (5 mL) was added an aqueous HI solution (0.49 mmol, 63 μL) at -30°C . The system was stirred at room temperature to give a pale yellow homogeneous solution. After the solution was stirred for 2 h, dichloromethane (5 mL) was added to the system. The organic layer was separated, dried over MgSO_4 , and concentrated to dryness to yield a pale yellow solid, which was recrystallized from acetone to give white crystals of **3** (0.28 g, 87%): ^1H NMR (C_6D_6 , room temperature) δ 0.71 (quintet, $J = 8.0$ Hz, 6 H, PCH_2CH_3), 0.78 (quintet, $J = 8.0$ Hz, PCH_2CH_3), 1.64–2.24 (m, 8 H, PCH_2CH_3), 2.02 (s, 3 H, CH_3 in *m*-tolyl); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , room temperature) 16.1 (s). Anal. Calcd for $\text{C}_{27}\text{H}_{37}\text{IP}_2\text{Pd}$: C, 49.4; H, 5.7; I, 19.3. Found: C, 49.2; H, 5.9; I, 19.5.

Kinetic Studies. A Schlenk tube containing a benzene solution (1.0 mL) of **1** (0.10 mmol) and MeI (2.0 mmol) was sealed with a gas-tight rubber cap under argon atmosphere. The Schlenk tube was placed in a thermostated bath (HAAKE F2) controlled to $50.0 \pm 0.1^\circ\text{C}$. The amounts of *m*-xylene and 3,3'-bitolyl produced with time were measured by means of HPLC using mesitylene (10 μL) as an internal standard. The system was homogeneous throughout the reaction, and no organic product other than *m*-xylene and 3,3'-bitolyl was detected. After completion of the reaction in half a day, the reaction yielded 75% / 1 of *m*-xylene and 25% of 3,3'-bitolyl. The solution was transferred into an NMR sample tube and examined by means of $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The ^{31}P NMR spectrum measured at room temperature exhibited three singlet signals at 24.8, 16.1, and 10.9 ppm in a ratio of 21:77:2. The former two peaks were assigned to **2** and **3**, respectively, while the latter was assigned to *trans*- $\text{PdI}_2(\text{PEt}_2\text{Ph})_2$ by comparison with the spectra of authentic samples.

The reaction was followed also by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at 50°C in C_6D_6 in vacuo. Initially, the ^{31}P NMR spectrum exhibited one singlet due to **1** at 19.8 ppm. On progress of the reaction the signal due to **1** decreased with increase of two singlets due to **2** and **3**. No signal other than those of **1**–**3** was observed throughout the reaction.

The reactions of **1** and MeI in the presence of added **2** were similarly examined by means of HPLC. First-order rate constants for *m*-xylene formation in the reactions of **1** (0.10 M) and **2** (0.30 M) at 50°C in benzene containing three different concentrations of MeI $10^4 k_{\text{obsd}}$, s^{-1} ([MeI], M) = 3.6 (1.0), 3.5 (1.5), and 3.7 (2.0).

The reaction of **1** (0.10 M) and MeI (2.0 M) in benzene containing PEt_2Ph (0.20 M) was followed by HPLC at 50°C . The half-life of **1** ($t_{1/2}$) in the reaction was derived from time-yield curves for *m*-xylene and 3,3'-bitolyl formation as 245 min as compared with $t_{1/2} = 115$ min for the reaction without free PEt_2Ph . The reaction solution examined by means of $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy after completion of the reaction showed three singlet peaks at 16.1, 24.8, and 38.8 ppm. The former two singlets were assigned to **3** and **2**, respectively, while the latter singlet was assigned to $[\text{PEt}_2(\text{Me})\text{Ph}]\text{I}$ by comparison with the spectra of authentic samples. The relative intensity of the sum of the signals due to **2** and **3** was same as that of the signal due to the phosphonium salt. No signal arising from free PEt_2Ph was detected.

Deuterium-Labeling Study. The reaction of **1** (0.10 M), CD_3I (2.0 M, isotopic purity, 99%), and/or **2** (0.10–0.50 M) was carried out in benzene at 50°C . After completion of the reaction, the reaction solution was collected by a trap to trap distillation and *m*-xylene produced was analyzed by GC-mass spectrometry. Relative ratio of nondeuterio- to trideuterio-*m*-xylene in the reaction solution was estimated on the basis of the authentic spectra of nondeuterio- and trideuterio-*m*-xylenes and mass spectra of 1:1 and 1:2 mixtures of standard samples of nondeuterio- and trideuterio-*m*-xylenes. The nondeuterio-*m*-xylene employed for the standard was the ordinary *m*-xylene from Wako Chemicals, while trideuterio-*m*-xylene was prepared by the cross-coupling reaction of *m*- $\text{CH}_3\text{C}_6\text{H}_4\text{I}$ and CD_3MgI in the presence of palladium catalyst.³ The results of mass spectroscopic analysis were reproducible within $\pm 5\%$.

Reaction of **1 and **2** in the Absence of MeI.** To a Schlenk tube containing **1** (0.10 mmol) and **2** (0.10 mmol) was added benzene (1.0 mL) containing dimethyl maleate (dmm, 0.20 mmol). The system was evacuated by pumping, and the tube was placed in a thermostated bath controlled to $60.0 \pm 0.1^\circ\text{C}$. At intervals, the Schlenk tube was removed from the bath and quickly cooled with liquid N_2 . The system was warmed to ca. 5°C , and the solution was analyzed by HPLC using mesitylene as an internal standard. The system was again evacuated and placed in the thermostated bath, and the reaction was resumed. The result is shown in Figure 4.

The reaction was examined also by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy under the same reaction conditions. Initially, the ^{31}P NMR spectrum exhibited two singlet peaks due to **1** and **2** at 19.7 and 24.0 ppm (at 60°C), respectively. On progress of the reaction, these signals decreased at similar rates accompanied by increase of signals due to **3**, $\text{Pd}(\text{dmm})(\text{PEt}_2\text{Ph})_2$, and $\text{Pd}(\text{dmf})(\text{PEt}_2\text{Ph})_2$ (dmf = dimethyl fumarate) at 15.6, 22.4, and 21.4 ppm.⁴ After ca. 30% conversion of **1**, the decreasing rate of **2** became slower than that of **1**. At the final stage, where the signal due to **1** was absent, the signals due to **2**, **3**, and $\text{Pd}(\text{O})$ -olefin complexes were observed in a ratio of 15:85:100, the ratio being in agreement with the result derived from HPLC analysis (Figure 4).

On the other hand, in the absence of dmm the reaction system rapidly darkened at 60°C and gave 97% / 1 of 3,3'-bitolyl and 3% of *m*-xylene, indicating occurrence of rapid thermolysis of **1**. Complex **1** was found to be fairly stable in solution at 60°C . The results suggest that rapid reductive elimination of bitolyl is induced by Pd^0 - PEt_2Ph species, which is afforded by the reaction of **1** and **2**. Indeed, thermolysis of **1** was markedly accelerated by addition of *trans*- $\text{PdEt}_2(\text{PEt}_2\text{Ph})_2$, which readily gives $[\text{Pd}(\text{PEt}_2\text{Ph})_2]$ species.¹¹ Thermolysis of **1** was effectively blocked by addition of a trapping reagent of $[\text{Pd}(\text{PEt}_2\text{Ph})_2]$ species, such as dmm. Addition of dmm, however, retarded also the reaction of **1** and **2**. Thus, direct comparison of reaction rates between reactions **1** and **2** could not be made. Dependence of $t_{1/2}$ of **1** on the concentration of dmm is as follows (reaction conditions, $[\text{1}] = [\text{2}] = 0.1$ M, at 60°C , in benzene): $t_{1/2}$, min ([dmm], M) = 220 (0.20), 135 (0.10), and 110 (0.06).

Appendix

Theoretical values for deuterium-labeling experiments were estimated as follows.

(9) In the absence of styrene color of the system turned red on stirring at -30°C and complex **1** could not be obtained. Styrene may serve as a trapping reagent for the Pd^0 - PEt_2Ph species that promotes rapid decomposition of **1** (see Experimental Section).

(10) Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319.

(11) (a) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. (b) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *168*, 375.

If one assumed that $2-d_0$ and $2-d_3$ have the same reactivity toward 1 (k_A and $k_B = k$), the decreasing rate of 1 in Scheme III is expressed as

$$-\frac{d[1]}{dt} = k[1]([2-d_0] + [2-d_3]) \quad (6)$$

Since in the presence of added 2 the side reaction affording 2 and 3,3'-bitolyl in reaction 1 can be ignored, the total concentration of $2-d_0$ and $2-d_3$ in Scheme III is maintained at the initial concentration of added 2, i.e., $[2-d_0] + [2-d_3] = [2]_{ad}$. Thus, eq 6 can be expressed as follows:

$$-\frac{d[1]}{dt} = k[1][2]_{ad} \quad (7)$$

From eq 7, the concentration of 1 at time t is derived as

$$[1] = [1]_0 \exp(-k[2]_{ad}t) \quad (8)$$

where $[1]_0$ stands for the initial concentration of 1. On the other hand, in Scheme III the decreasing rate of $2-d_0$ can be expressed as

$$-\frac{d[2-d_0]}{dt} = k[1][2-d_0] \quad (9)$$

From eq 8 and 9

$$-\frac{d[2-d_0]}{dt} = k[1]_0 \exp(-k[2]_{ad}t)[2-d_0] \quad (10)$$

From eq 10 the concentration of $2-d_0$ at time t is given as follows:

$$[2-d_0] = [2]_{ad} \exp \left[\frac{[1]_0}{[2]_{ad}} \{ \exp(-k[2]_{ad}t) - 1 \} \right] \quad (11)$$

Since the concentration of nondeuterio- m -xylene at time t ($[ArCH_3]$) is given by

$$[ArCH_3] = [2]_{ad} - [2-d_0] \quad (12)$$

the following equation is derived from eq 11 and 12:

$$[ArCH_3] = [2]_{ad} \left[1 - \exp \left\{ \frac{[1]_0}{[2]_{ad}} (\exp(-k[2]_{ad}t) - 1) \right\} \right] \quad (13)$$

Thus

$$\lim_{t \rightarrow \infty} [ArCH_3] = [2]_{ad} \left\{ 1 - \exp \left(-\frac{[1]_0}{[2]_{ad}} \right) \right\} \quad (14)$$

On the other hand

$$\lim_{t \rightarrow \infty} [ArCD_3] + \lim_{t \rightarrow \infty} [ArCH_3] = [1]_0 \quad (15)$$

where $[ArCD_3]$ stands for the concentration of tri-deuterio- m -xylene at time t . From eq 14 and 15

$$\lim_{t \rightarrow \infty} [ArCD_3] = [1]_0 - [2]_{ad} \left\{ 1 - \exp \left(-\frac{[1]_0}{[2]_{ad}} \right) \right\} \quad (16)$$

Theoretical values for the ratio of trideuterio- to nondeuterio- m -xylene at the end of the reaction ($\lim_{t \rightarrow \infty} ([ArCD_3]/[ArCH_3])$) can be derived from eq 14 and 16.

Registry No. 1, 104114-85-4; 2, 104114-86-5; 3, 104114-87-6; $PdBr_2(P(Et_2Ph)_2)$, 53996-89-7; *trans*- $PdMe_2(P(Et_2Ph)_2)_2$, 77831-30-2; Me I, 74-88-4; m -xylene, 108-38-3; 3,3'-bitolyl, 612-75-9.

Communications

Electrochemical Generation and Reactivity of Bis(triethylphosphine)platinum(0): Formation of a Platinum Hydride via a Hoffman Elimination Reaction with the Tetra- n -butylammonium Cation

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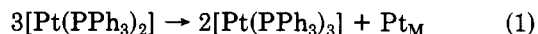
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Received March 20, 1986

Summary: Controlled potential bulk reductive electrolysis of *cis*- $[PtCl_2(P(Et_3)_2)_2]$ at a mercury pool electrode in acetonitrile/benzene (5/2) solution containing tetra- n -butylammonium perchlorate results in the generation of $[Pt(P(Et_3)_2)_2]$. This two-coordinate, 14-electron complex acts as a base under specific reaction conditions to abstract a β -H from the tetra- n -butylammonium cation initiating a Hoffman degradation and subsequently forming *trans*- $[PtH(Cl)(P(Et_3)_2)_2]$ after reattack of Cl^- . Under different reaction conditions, other basic/nucleophilic chemistry of $[Pt(P(Et_3)_2)_2]$ is observed which includes reactions with weakly activated C-H and/or C-C σ bonds.

We have previously shown¹ that the controlled potential

bulk reductive electrolysis of *cis*- $[PtCl_2(PPh_3)_2]$ produces a two-coordinate, 14-electron complex, $[Pt(PPh_3)_2]$.² This complex can be trapped by stoichiometric quantities of acetylenes ($RC \equiv CR$; $R = Ph, COOMe$) and oxidized to Pt(II) by the addition of small molecules such as MeI and $PhCOCl$. In the absence of trapping agents, disproportionation is observed (eq 1). The $[Pt(PPh_3)_2]$ complex



does not undergo any meaningful reaction chemistry with the C-H or C-C bonds present in the components of the solvent system (5/2 acetonitrile/benzene) or with the background electrolyte (tetra- n -butylammonium perchlorate, TBAP) used in the electrolysis.¹

To increase the reactivity of the 14-electron species,² triphenylphosphine was replaced by the more powerful σ donor triethylphosphine. The basicity of triethylphosphine is anticipated to cause the electron density at the metal center to be greater than in the triphenylphosphine ana-

(1) Davies, J. A.; Eagle, C.; Otis, D. E.; Venkataraman, U. *Organometallics* 1986, 5, 1264.

(2) It is possible that the Pt(0) species is stabilized through weak coordination of benzene or acetonitrile solvent molecules. This type of solvation would not be excluded for $[Pt(P(Et_3)_2)_2]$. Troglor has postulated this type of solvation by benzene (see ref 5), and solvation by hard donor solvents has also been postulated for $[Pt(PPh_3)_2]$; see: Siedle, A. R.; Newmark, R. A.; Gleason, W. R. *J. Am. Chem. Soc.* 1986, 108, 767.