Synthesis and Properties of Cationic Organopalladium Complexes. Remarkable Rate Enhancement in Olefin Insertion into the Palladium–Aryl Bond by the Generation of a Cationic Palladium Complex from *trans*-[PdBr(Ph)(PMe_3)$_2$]

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By removing the bromide ligand in *trans*-[PdBr(Ph)(PMe_3)$_2$] (**1**) by $AgBF_4$ in the presence and absence of pyridine, pyridine-coordinated and solvent-coordinated cationic complexes, *trans*-[PdPh(py)(PMe_3)$_2$]BF_4 (**2**) and *trans*-[PdPh(solvent)(PMe_3)$_2$]BF_4 (**3**), have been obtained. These cationic phenylpalladium complexes show much greater reactivities than do the parent neutral complex **1** toward olefins to give phenylated olefins by insertion followed by β-hydrogen elimination processes. Kinetic studies concerning the insertion of methyl acrylate into the phenyl-palladium bond have indicated that the reactions are first order in the phenylpalladium complexes and that addition of pyridine to a system containing **2** and methyl acrylate inhibits the insertion reaction of the olefin. The results suggest that the generation of a cationic arylpalladium complex with a vacant site is important for the olefins to be inserted.

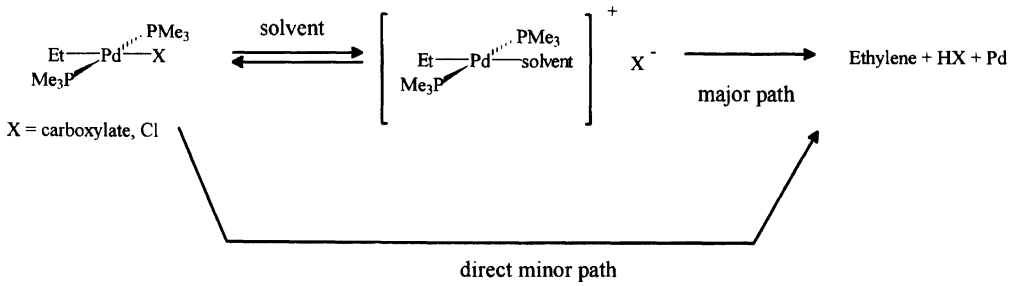
The arylation of olefins with aryl halides catalyzed by palladium complexes developed by Mizoroki[1] and Heck[2] has been extensively used in organic synthesis.[3] The catalytic cycle has been considered to comprise the following elementary steps: (a) oxidative addition of aryl halide to a Pd(0) complex to give an arylpalladium halide species, (b) insertion of olefin into the aryl–Pd bond, (c) a subsequent β-hydrogen elimination to give hydridopalladium halide, and (d) dehydrohalogenation by a base to regenerate the Pd(0) species that carries the catalytic cycle.[4]

However, fundamental studies concerning the elementary processes of organopalladium complexes that are assumed to act as intermediates in the catalytic process have been quite limited until recently. Milstein's group dealt with the insertion of styrene into phenyl–palladium complexes with special chelating phosphines,[5] and Cheng's group reported on the insertion of norbornadiene into a Ph–Pd complex having triphenylphosphine ligands.[6]

During the course of our studies on the reactivities of organopalladium complexes[7,8] we found that isolated trimethylphosphine-coordinated monoethylpalladium complexes having electronegative ligands are thermolyzed via a route involving the dissociation of the electronegative ligand in solution as a main decomposition pathway (Scheme 1).[8a]

The result suggested that a cationic organopalladium complex generated by the dissociation of the anionic ligand is more reactive than the parent neutral monoorganopalladium complex. In fact, the monoethylpalladium complex produced by removing the halide ligand X from *trans*-[PdEt(X)(PMe_3)$_2$] with a silver ion proved to be very susceptible to β-hydrogen elimination.[8a] The results prompted us to study the chemistry of various cationic monoorganopalladium complexes in order to compare their behavior with that of the corresponding neutral organopalladium complexes.

Recently, the effect of silver salts added to the catalytic Heck processes has attracted considerable interest.[9—15] The addition of silver salts often causes an enhancement in the reaction rate, and sometimes even improves the selectivity of Heck-type reactions. It has also been noted that the use of aryl and alkenyl triflates in combination with Pd(0) catalysts facilitates Heck reactions.[16,17] These results implicate an involvement of cationic organopalladium complexes having higher reactivities than the corresponding neutral complexes in the catalytic Heck processes. We report here on the preparation and characterization of cationic phenylpalladium complexes having trimethylphosphine ligands, and give a quantitative comparison of their enhanced reactivities toward various olefins which undergo insertion into the Pd–Ph bond and subsequent β-hydrogen elimination to liberate phenylated olefins.



Scheme 1.

Experimental

General Procedure. All of the manipulations of the complexes were performed under argon using Schlenk flasks. *cis*-[$PdCl_2(PMe_3)_2$] was prepared as reported in the literature.[18] Trimethylphosphine and the other reagents were purchased and used as received.

Elemental analyses were carried out using a Yanako MT-3. The NMR spectra were recorded on a Hitachi R-90H (^1H, 90.055 Hz) or a JEOL EX-270 spectrometer (^1H, 270.166 MHz; ^{31}P, 109.381 MHz). ^1H signals are referred to Me_4Si as an internal standard, and ^{31}P NMR signals to 85% H_3PO_4 as an external reference. IR spectra were recorded on a Hitachi I-3000 spectrophotometer. Preparative methods of the new palladium complexes are described below.

Preparation of *trans*-[PdPh(Br)(PMe_3)$_2$] (1). A THF solution of PhMgBr (0.2 mol dm^{-3}, 5.5 mL, 0.11 mmol) was added to a THF (2 mL) solution containing *cis*-[$PdCl_2(PMe_3)_2$] (91 mg, 0.028 mmol) and PMe_3 (14 μL, 0.022 mmol) at −20 °C. Stirring the reaction mixture for 30 min gave a colorless solution. After evaporation of the solvent, the remaining PhMgBr was quenched with aq NH_4Cl. White powder of *trans*-[PdBr(Ph)(PMe_3)$_2$] was extracted with CH_2Cl_2 and recrystallized from acetone and Et_2O to afford 41 mg of light-yellow crystals (0.011 mmol, 39% yield), mp 173—175 °C (decomp). Anal. Calcd for $C_{12}H_{23}BrP_2Pd$: C, 34.7; H, 5.6%. Found: C, 34.4; H, 5.7%. ^1H NMR ($CDCl_3$) δ=1.21 (vt, 18H, 3.8 Hz), 6.95—7.13 (m, 3H, *m*, *p*-C_6H_5) and 7.2—7.34 (m, 2H, *o*-C_6H_5). ^{31}P NMR ($CDCl_3$) δ=−17.0 (s). IR (KBr) 1564, 1418, and 950 cm^{-1}.

Preparation of *trans*-[PdPh(py)(PMe_3)$_2$]BF_4 (2). An acetone solution (1.0 mL) containing silver tetrafluoroborate (191 mg, 0.981 mmol) and pyridine (1.0 mL, 12 mmol) was added to a CH_2Cl_2 (9.8 mL) solution of *trans*-[PdBr(Ph)(PMe_3)$_2$] (408 mg, 1.1 mmol) at −60 °C. After stirring the reaction mixture for 1 h at −20 °C, produced silver bromide was removed by filtration. Evaporation of the solvent and pyridine from the filtrate left a white solid of *trans*-[PdPh(py)(PMe_3)$_2$]BF_4, which was recrystallized from acetone and Et_2O to afford 423 mg of colorless crystals (0.84 mmol, 86% yield), mp 123—124 °C (decomp). Anal. Calcd for $C_{17}H_{28}NP_2Pd$: C, 40.7; H, 5.6; N, 2.8%. Found: C, 40.6; H, 5.8; N, 2.9%. ^1H NMR (acetone-d_6) δ=1.03 (vt, 18 H, PC*H*$_3$), 6.9—7.2 (m, 3 H, C_6H_5), 7.35—7.52 (m, 2H, C_6H_5), and 7.62—7.85 (m, 2H, NCHC*H*), 8.00—8.24 (m, 1H, NCHCHC*H*), and 8.90—9.10 (m, 2H, NC*H*). ^{31}P NMR ($CDCl_3$) δ=−18.3 (s). IR (KBr) 1564, 1036, 956 cm^{-1}.

Preparation of *trans*-[PdPh(solvent)(PMe_3)$_2$]BF_4 (3) *in situ*. An acetone-d_6 solution of silver tetrafluoroborate (0.15 mL, 0.09 mol dm^{-3}, 0.014 mmol) was added to a CD_2Cl_2 (0.3 mL, 0.045 mol dm^{-3}, 0.015 mmol) solution of *trans*-[PdBr(Ph)(PMe_3)$_2$] at −30 °C. Only one kind of species was observed by NMR.

^1H NMR (CD_2Cl_2 : acetone-d_6=2 : 1) δ=1.07 (vt, 18H, J= 3.0 Hz), 6.8—7.0 (m, 3H, *m*, *p*-C_6H_5) and 7.1—7.3 (m, 2H, *o*-C_6H_5). ^{31}P NMR (CD_2Cl_2 : acetone-d_6 = 2 : 1) δ = −17.9 (s).

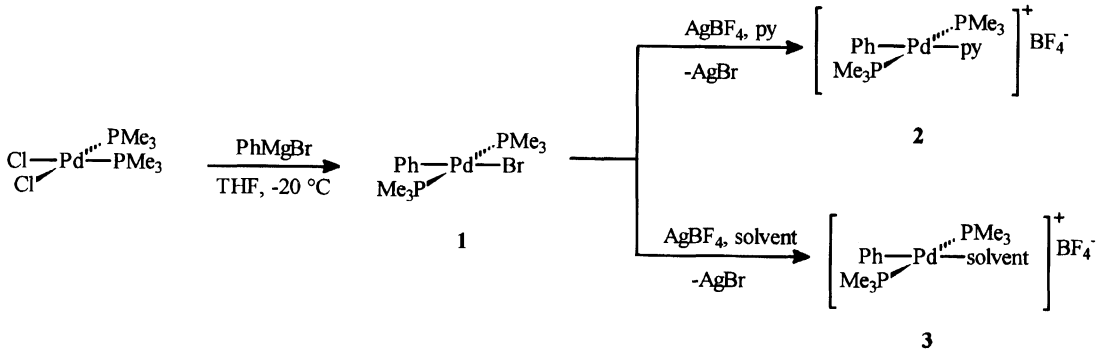
Reaction of 1 with Methyl Acrylate. Five equivalents of methyl acrylate were added to an acetonitrile solution of complex **1** (108 mg, 0.260 mmol). After refluxing the reaction mixture for 3 h, the formation of benzene (0.48 equiv/Pd) and methyl cinnamate (0.49 equiv/Pd) was confirmed by a GLC analysis. *cis*-[$PdBr_2(PMe_3)_2$] (35 mg, 0.33 equiv/Pd) was isolated by column chromatography and was identified by a comparison with a sample prepared from *cis*-[$Pd(CH_3CN)_2Br_2$] and PMe_3.[19]

Kinetic Studies of the Reactions of the Cationic Phenylpalladium Complexes with Olefins. Method A. NMR samples containing a fixed concentration (0.03 mol dm^{-3}) of *trans*-[PdPh(py)(PMe_3)$_2$]BF_4 (**2**) and *trans*-[PdPh(solvent)(PMe_3)$_2$]BF_4 (**3**) and various concentrations of additives were prepared. The ^1H NMR spectra of the samples were periodically observed at several preset temperatures. By following the decrease in the concentrations of **2** or **3** or the increase in the arylated olefins with time by NMR, the reactions were established to follow first-order kinetics. The k_{obsd} values were obtained from the slope of the log plot of the concentrations of the complexes vs. time.

Method B. Samples containing **2** and **3** (0.03 mol dm^{-3}) and additives in various concentrations were prepared. The yields of phenylated olefins produced in the systems were periodically measured at several preset temperatures by GLC analysis. The k_{obsd} values were determined by measuring the amounts of phenylated olefins formed as a function of time.

Results

1. Preparations of *trans*-[PdBr(Ph)(PMe_3)$_2$] (1), *trans*-[PdPh(py)(PMe_3)$_2$]BF_4 (2), and *trans*-[PdPh(solvent)(PMe_3)$_2$]BF_4 (3). *trans*-[PdBr(Ph)(PMe_3)$_2$] (**1**) was prepared by treating *cis*-[$PdCl_2(PMe_3)_2$] with four equivalents of PhMgBr in THF at −20 °C. Removal of the bromide ligand from **1** in a CH_2Cl_2 solution with an equiv. of $AgBF_4$ in the presence of an excess of pyridine afforded *trans*-[PdPh(py)(PMe_3)$_2$]BF_4 (**2**). These complexes were characterized by IR, NMR, and elemental analysis. The treatment of **1** in dichloromethane with an acetone solution



Scheme 2.

of 1 equiv of $AgBF_4$ provided a single species that has been characterized by NMR as *trans*-[PdPh(solvent)-$(PMe_3)_2$]BF_4 (**3**) (Scheme 2). Since the isolation of **3** was not feasible, a solvent-coordinated cationic phenylpalladium complex generated *in situ* was used for further reactions. An NMR examination of **3** indicated the retainment of the *trans* configuration, as evidenced by the appearance of a virtual triplet signal for the PMe_3 ligands in **3**.

2. Kinetic Study of the Reactions of the Phenylpalladium Complexes 1, 2, and 3 with Various Olefins. Comparison of the reactivities of the neutral, pyridine-coordinated cationic, and solvent-coordinated cationic phenylpalladium complexes **1**—**3** toward olefins indicated that the neutral complex **1** is much less reactive than the cationic complexes, and that the pyridine-coordinated complex **2** is less reactive than the solvent-coordinated complex **3** prepared *in situ* by removing the bromide ligand from **1** in an acetone–dichloromethane solution. For example, the neutral complex did not react with methyl acrylate at 50 °C, and it was required to heat the system to above 70 °C to carry out a reaction with methyl acrylate, whereas the pyridine-coordinated complex **2** reacted with methyl acrylate smoothly at 40 °C. In contrast, **3** is thermally unstable and a kinetic study of **3** with methyl acrylate was necessary to be performed at 5 °C.

The reaction of **2** with methyl acrylate cleanly produced one equiv. of methyl cinnamate. On the other hand, the reaction of **1** with the same olefin above 70 °C produced 0.5 equiv each of methyl cinnamate and benzene together with the formation of 0.43 equiv of *cis*-[$PdBr_2(PMe_3)_2$], whereas the addition of amine gave methyl cinnamate quantitatively without releasing benzene. The solvent-coordinated complex **3** also released 0.5 equiv each of benzene and methyl cinnamate, as confirmed by GLC and column chromatography, respectively.

Benzene formation in reactions of the phenyl palladium complexes with olefins is ascribed to the protonolysis of the phenylpalladium complexes **1** and **3** by HBr or HBF_4 formed by olefin insertion and a subsequent β-hydrogen elimination. In the presence of pyridine or amine the proton is trapped before attacking the phenylpalladium species to liberate benzene.

The reaction courses of the neutral and cationic phenylpalladium complexes with olefins were followed by observing the disappearance of the phenylpalladium complexes by NMR, and by following the formation of methyl cinnamate by GLC. The results showed that the reaction of **3** with methyl acrylate or styrene to produce methyl cinnamate or stilbene in various concentrations of the acrylate or styrene is first order in the concentration of the phenylpalladium complex.

A plot of the observed first-order rate constant (k_{obsd}) versus the concentration of the added methyl acrylate and styrene gave Fig. 1. Figure 1 shows that the first-order rate constant increases only slightly along with an increase in the olefin concentration. The rate of reaction of the pyridine-coordinated complex **2** with methyl acrylate to release methyl cinnamate also follows first-order kinetics. The addition of pyridine to the reac-

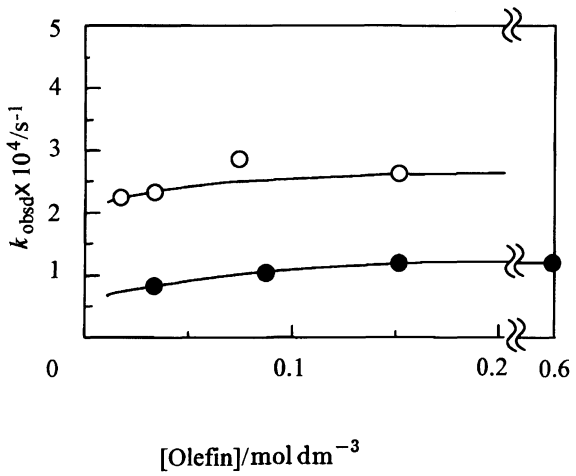


Fig. 1. Relation between concentration of added olefins and reaction rate. $[3]_{t=0} = 0.03$ mol dm^{-3}. Solvent=CH_2Cl_2 : acetone (2 : 1). Temp=5 °C. ○= Methyl acrylate, ●=Styrene.

tion system strongly inhibits the reaction, as shown in Fig. 2, where the observed first-order rate constant (k_{obsd}) is plotted against the concentration of pyridine added, [py]. No reaction of **2** with methyl acrylate was observed in a neat pyridine solution. The reciprocal plot of k_{obsd} vs. [py] gives a linear plot, as shown in Fig. 3. The first-order rate constant (k_{obsd}) in the reaction of **2** with methyl acrylate in the presence of pyridine can be expressed as

$$k_{obsd}/s^{-1} = \frac{66 \times 10^{-5}}{1 + 26[\text{pyridine}]/\text{mol dm}^{-3}}. \quad (1)$$

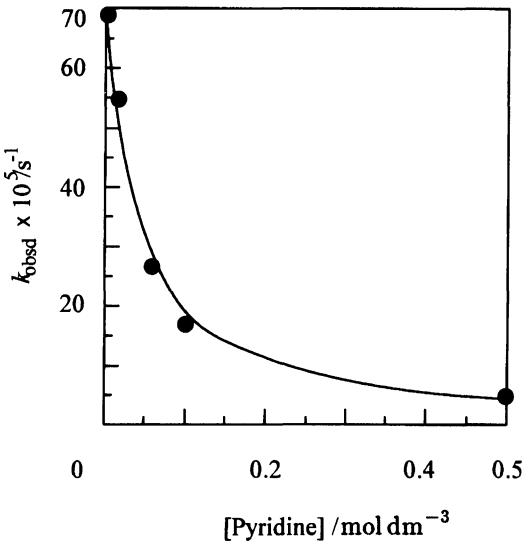


Fig. 2. Correlation between pyridine added and k_{obsd} in the reaction of complex **2** with methyl acrylate. $[\mathbf{3}]_{t=0} = 0.03$ mol dm^{-3}. Solvent = CH_2Cl_2 : acetone (2 : 1). Temp=5 °C.

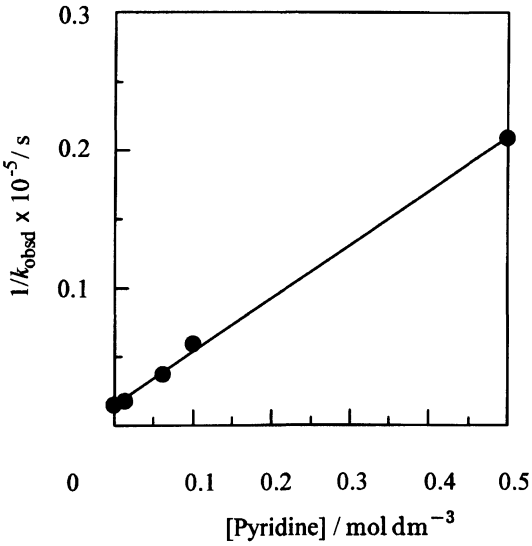


Fig. 3. Correlation between pyridine added and $1/k_{obsd}$ in the reaction of complex **2** and methyl acrylate. $[\mathbf{2}]_{t=0} = 0.03$ mol dm^{-3}. Solvent = CH_2Cl_2 : acetone (2 : 1). Temp=5 °C.

3. Reactions of the Cationic Phenylpalladium Complex 3 with Other Olefins. Table 1 summarizes the results of reactions of **3** with various olefins. In general, olefins with electron-withdrawing substituents are more reactive than olefins with electron-releasing substituents. The reactions of **3** with unsubstituted ethylene, methyl acrylate, and methyl vinyl ketone were completed within 2 h at 5 °C, whereas the reactions with styrene needed about 3 h and 1-octene needed more than 5 h to be completed at the same temperature. The rate of reaction of methyl crotonate with **3** was 38% of that of methyl acrylate. 1,1-Diphenylethylene and stilbene were unreactive at the temperature.

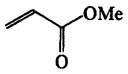
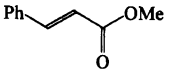
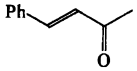
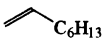
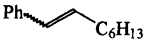
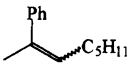
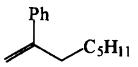
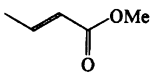
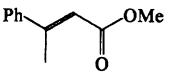
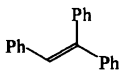
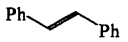
Discussion

The obtained results indicate that the cationic phenylpalladium complex generated by removing the bromide ligand from **1** with a silver salt is much more reactive than the neutral, parent complex **1**. In the presence of a base the reaction cleanly proceeds by olefin insertion into the Ph–Pd bond and the subsequent β-hydrogen elimination processes to liberate the phenylated olefin. On the other hand, in the absence of a base the phenylpalladium complex **1** is decomposed immediately after HBr is produced in β-hydrogen abstraction. The formation of half an equiv each of benzene and *cis*-$[PdBr_2(PMe_3)_2]$ suggests the reaction process shown in Scheme 3. In the reaction of the pyridine-coordinated complex **2** with methyl acrylate, pyridine effectively traps the formed protic acid. The clear inhibition effect of added pyridine in the reaction with methyl acrylate suggests that a coordination site is necessary for the insertion of methyl acrylate into the phenyl–palladium bond to proceed. The kinetic results may be accommodated by assuming the reaction sequence shown in Scheme 4. The scheme is reminiscent of the kinetic expression obtained in the thermolysis of *trans*-$[PdEt(X)(PMe_3)_2]$ (Scheme 1), where X is an electronegative ligand, such as a halide or carboxylate.[8a] The replacement of the coordinated pyridine ligand by the assistance of the solvent molecule generates a solvent-coordinated cationic phenylpalladium complex (**3**). The subsequent coordination of the olefin followed by its insertion into the Ph–Pd bond and β-hydrogen elimination liberates methyl cinnamate. The assumption of a steady state for the cationic solvent-coordinated complex **3** and the subsequent fast steps, possibly involving replacement of the coordinated solvent by the olefin, leads to the kinetic expression of Eq. 2, which is in agreement with the experimental result expressed by Eq. 1.

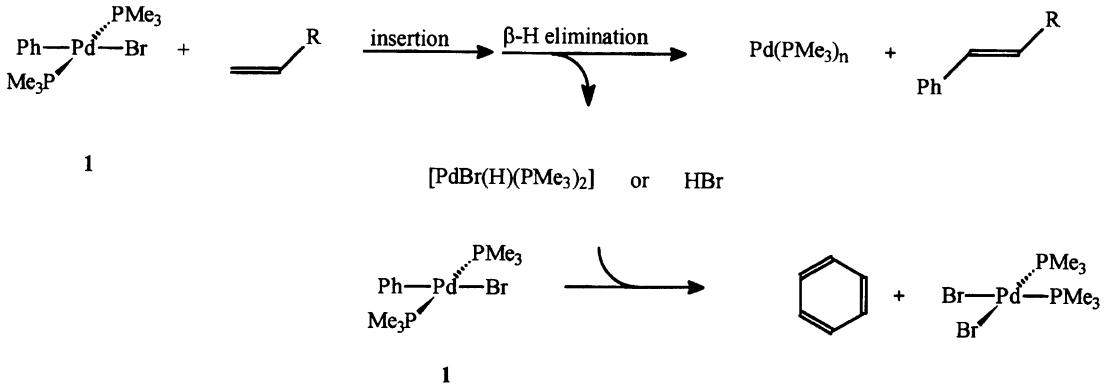
$$k_{obsd} = \frac{k_1 k_2}{k_{-1}[\text{py}] + k_2}. \quad (2)$$

The results of kinetic studies on the reaction of the solvent-coordinated complex **3** with various olefins revealed that the reaction is first order in the concentration of **3**, and that the observed first-order rate constant

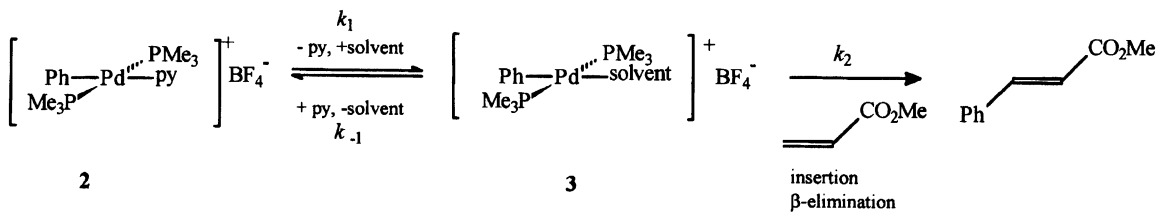
Table 1. Rate Constants of Reaction between **3** and Various Olefins

Substrates	Products (aryl olefins)	Yields/%	$k_{obsd} \times 10^5/s^{-1}$
$H_2C=CH_2$ (1 atm, 5 equiv)		49	27.2
		49	23.8
		49	21.8
		33	12.8
		1	
		9	
		33	3.5
		3	
		13	
		43	9.2
		Trace	
		N.R.	

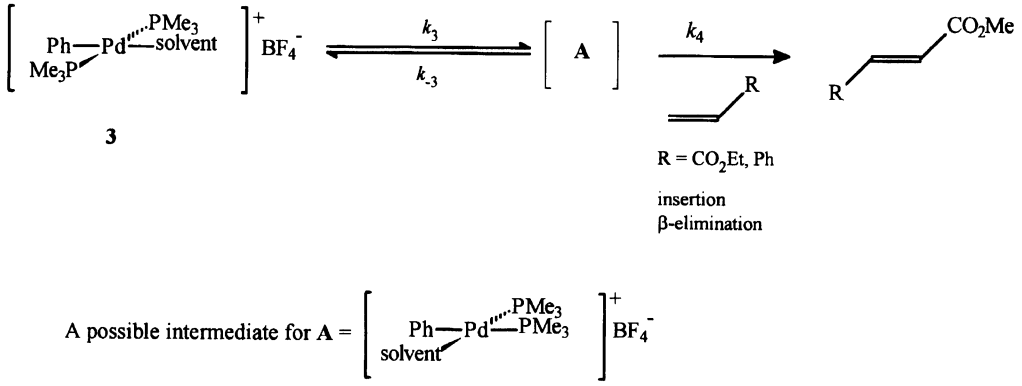
$[\mathbf{3}]_{t=0} = 0.03$ mol dm^{-3}, concentrations of olefins except ethylene $= 0.15$ mol dm^{-3}, solvent=acetone : $CH_2Cl_2 = 1:2$, reaction temperature=5 °C. Benzene was also observed by GLC analysis.



Scheme 3.



Scheme 4.



Scheme 5.

increases only slightly along with an increase in the concentration of olefin (Fig. 1). An NMR examination of a system containing **3** and methyl acrylate (5 equiv) in acetone indicated no formation of the olefin–palladium complex at −60, −30, −15, and 5 °C. Thus, the olefin coordination to the phenylpalladium complex is considered not to be involved in the pre-equilibrium step. Scheme 5 shows a mechanism to accommodate these experimental results.

In this mechanism the solvent-coordinated complex **3** is converted into an unstable complex **A** which is then attacked by olefin to undergo the insertion and β-hydrogen elimination processes to produce the phenylated olefin. A steady state assumption for intermediate **A** leads to the following rate expression:

$$k_{\text{obsd}} = \frac{k_3 k_4[\text{olefin}]}{k_{-3} + k_4[\text{olefin}]}. \quad (3)$$

If k_{-3} is much greater than k_4[olefin], the k_{obsd} value is expressed by

$$k_{\text{obsd}} = \frac{k_3 k_4[\text{olefin}]}{k_{-3}}. \quad (4)$$

If k_{-3} is much smaller than k_4[olefin], k_{obsd} is reduced to k_3, independent of the olefin concentration. As shown by Fig. 1, the rate constant increases slightly along with an increase in the olefin concentration, and is independent of the olefin concentration in the higher olefin concentration range. The results are in agreement with Scheme 5.

Establishing the identity of complex **A** is not feasible, since **A** is an unstable intermediate and is not observable by spectroscopic means. We consider that a likely candidate for **A** is the *cis* isomer of **3**, which undergoes further olefin coordination the subsequent insertion followed by a β-hydrogen elimination.

In the olefin insertion step the phenyl ligand and the olefin to be inserted are required to be in adjacent positions. This situation can be achieved if the phosphine ligands do not dissociate, by approaching the olefin from above or below the molecular plane; however a considerable steric interaction is expected for the olefin to approach a phenylpalladium complex flanked by two tertiary phosphine ligands. The other site adjacent to the phenyl ligand is in the molecular plane *cis* to the phenyl ligand, the site occupied by one of the PMe_3 ligands. In a study of the insertion of norbornadiene into a phenyl–palladium complex having two triphenylphosphine ligands Cheng et al.[6] indicated that one of the two PPh_3 ligands dissociates to make room for the coordination of the norbornadiene ligand that is inserted into the phenyl–palladium bond to give the insertion product. In the present case the trimethylphosphine ligand, being compact and basic, is not expected to dissociate readily from palladium, though a *trans* to *cis* isomerization may be a possible process to form **A**. The formation of *cis*-$PdBr_2(PMe_3)_2$ after olefin insertion and subsequent β-elimination steps (Scheme 3) suggests that the occurrence of such *trans–cis* isomerization is a viable process.

In the reaction of the pyridine-coordinated complex **2**, the solvent first replaces the pyridine ligand to give **3**, which then reacts to give **A**, which further undergoes insertion and subsequent β-hydrogen elimination.

In conclusion, the experimental results observed in the present study are compatible with the promotion effect by a silver ion in the Heck-type olefin arylation, and indicate the importance of generating a cationic arylpalladium complex. The present results are complementary with the reports of Cheng[6] and Milstein[5] in accounting for the mechanism of the Heck reaction.

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References

1) T. Mizoroki, K. Mori, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **44**, 581 (1971).

2) R. F. Heck and J. P. Nolley, *J. Org. Chem.*, **37**, 2320 (1972).

3) a) R. F. Heck, *Org. React. (N. Y.)*, **27**, 345 (1982); b) R. F. Heck, *Pure Appl. Chem.*, **53**, 23 (1981); c) R. F. Heck, *Acc. Chem. Res.*, **12**, 146 (1979); d) R. F. Heck, "Palladium

Reagents in Organic Synthesis," Academic Press, New York (1985); e) B. M. Trost and I. Fleming, "Comprehensive Organic Synthesis," Pergamon Press, New York (1991), Vol. 4.

4) a) J. P. Collmann, L. S. Hegedus, J. R. Norton, and R. R. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, CA (1987); b) R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals," Wiley, New York (1994); c) A. Salzer and Ch. Eschenbroich, "Organometallics A Concise Introduction," 2nd revised ed, VCH Publishers, New York (1992); d) A. Yamamoto, "Organotransition Metal Chemistry, Fundamental Concepts and Applications," Wiley Interscience, New York (1986).

5) a) Y. Ben-David, M. Portnoy, M. Gozin, and D. Milstein, *Organometallics*, **11**, 1995 (1992); b) M. Portnoy, Y. Ben-David, and D. Milstein, *Organometallics*, **12**, 4734 (1993).

6) C. S. Li, D. C. Jou, and C. H. Cheng, *Organometallics*, **12**, 3945 (1993).

7) a) A. Yamamoto, T. Yamamoto, S. Komiya, and F. Ozawa, *Pure Appl. Chem.*, **56**, 1621 (1984); b) A. Yamamoto, *J. Organomet. Chem.*, **300**, 347 (1986), and references cited therein.

8) a) F. Kawataka, Y. Kayaki, I. Shimizu, and A. Yamamoto, *Organometallics*, **13**, 3517 (1994); b) Y.-J. Kim, K. Osakada, A. Takenaka, and A. Yamamoto, *J. Am. Chem. Soc.*, **112**, 1096 (1990); c) K. Osakada, Y. Ozawa, and A. Yamamoto, *J. Chem. Soc., Dalton Trans.*, **1991**, 759; d) K. Osakada, Y. Ozawa, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **64**, 2002 (1991).

9) a) K. Karabelas and A. Hallberg, *Tetrahedron Lett.*, **26**, 3131 (1985); b) K. Karabelas, C. Westerlund, and A. Hallberg, *J. Org. Chem.*, **50**, 3896 (1985); c) K. Karabelas and A. Hallberg, *J. Org. Chem.*, **51**, 5286 (1986).

10) a) M. M. Abelman, T. Oh, and L. E. Overman, *J. Org. Chem.*, **52**, 4130 (1987); b) M. M. Abelman and L. E. Overmann, *J. Am. Chem. Soc.*, **110**, 2328 (1988).

11) a) T. L. Jeffery, *Tetrahedron Lett.*, **31**, 6641 (1990); b) T. L. Jeffery, *J. Chem. Soc., Chem. Commun.*, **1991**, 324; c) T. L. Jeffery, *Tetrahedron Lett.*, **33**, 1989 (1992).

12) a) R. C. Larock, H. Song, B. E. Baker, and W. H. Gong, *Tetrahedron Lett.*, **29**, 2919 (1988); b) R. C. Larock, W. H. Gong, and B. E. Baker, *Tetrahedron Lett.*, **30**, 2603 (1989); c) R. C. Larock and W. H. Gong, *J. Org. Chem.*, **54**, 2047 (1989).

13) a) W. Cabri, I. Candiani, A. Bedeschi, S. Penco, and R. Santi, *J. Org. Chem.*, **57**, 1481 (1992); b) W. Cabri, I. Candiani, A. Bedeschi, and R. Santi, *J. Org. Chem.*, **57**, 3558 (1992); c) W. Cabri, I. Candiani, A. Bedeschi, and R. Santi, *Tetrahedron Lett.*, **32**, 261 (1991).

14) a) Y. Sato, S. Watanabe, and M. Shibasaki, *Tetrahedron Lett.*, **33**, 2589 (1992); b) Y. Sato, T. Honda, and M. Shibasaki, *Tetrahedron Lett.*, **33**, 2593 (1992).

15) R. Grigg, V. Loganathan, V. Santhakumar, V. Sridharan, and A. Taesdale, *Tetrahedron Lett.*, **32**, 687 (1991).

16) W. J. Scott and J. E. McMurray, *Acc. Chem. Res.*, **1988**, 47, and references cited therein.

17) F. Ozawa, A. Kubo, and T. Hayashi, *J. Am. Chem. Soc.*, **113**, 1417 (1991).

18) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, **1938**, 702.

19) J. M. Jenkins and J. G. Verkade, *Inorg. Synth.*, **11**, 108 (1968).