

## Kinetics and Equilibrium of the Reaction between Bis(trifluoroacetylacetonato)palladium(II) and Tri-*o*-tolylphosphine

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Tri-*o*-tolylphosphine reacts with bis(trifluoroacetylacetonato)palladium(II), Pd(tfac)<sub>2</sub>, to convert one of the chelating ligands into the unidentate state, resulting in Pd(tfac)(tfac-*O*)P(*o*-tolyl)<sub>3</sub>. The reaction was studied by a spectrophotometric method. The equilibrium constant was determined at several temperatures, *K* being 1.38 × 10<sup>3</sup>, 4.35 × 10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> and more than 10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> in benzene, dichloromethane, and methanol, respectively, at 25 °C. In the presence of excess phosphine, the reaction proceeds as a pseudo first order reaction to attain equilibrium. The forward and reverse rate constants, *k*<sub>1</sub> and *k*<sub>-1</sub>, were obtained as 0.172 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and 1.22 × 10<sup>-4</sup> s<sup>-1</sup> in benzene and 2.28 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and 4.9 × 10<sup>-4</sup> s<sup>-1</sup> in dichloromethane at 25 °C, respectively. In methanol the forward rate was measured under irreversible pseudo first order conditions and conforms with the usual two term rate law, *k*<sub>obsd</sub>/s<sup>-1</sup> = 2 × 10<sup>-3</sup> + 56.6[P(*o*-tolyl)<sub>3</sub>]. The remarkable dependence of *K* and *k*<sub>1</sub> on the nature of solvent is related to the hydrogen bonding interaction between the carbonyl group of the coordinated tfac anion and a solvent molecule.

The kinetic study in a previous paper<sup>1)</sup> of the reactions between bis(acetylacetonato)palladium(II) and alkylamines (L) to afford the mixed-ligand cationic complexes of the [Pd(acac)L<sub>2</sub>](acac) type revealed that Pd(acac)(acac-C<sup>3</sup>)L is not an intermediate in this reaction but is formed *via* the above outer-sphere complex.\*\* A complex such as Pd(acac)(acac-*O*)L containing an *O*-unidentate acetylacetonate anion is then supposed to be involved as an intermediate in the reaction pathway, although it is not sufficiently accumulated to be detected spectrophotometrically.

Mercury(II)<sup>2,3)</sup> and silicon(IV)<sup>4,5)</sup> complexes containing an oxygen-bonded β-diketonate anion as a unidentate ligand have been reported. Recently the reactions of bis(acetylacetonato)platinum(II) with triethylphosphine<sup>6)</sup> at low temperature (< -10 °C) and with piperidine<sup>7)</sup> at 70 °C were found to give the Pt(acac-*O*)<sub>2</sub>-L<sub>2</sub> complexes. Similarly the reaction of dimethyl(acetylacetonato)gold(III) with tricyclohexylphosphine<sup>8)</sup> and reactions of bis(trifluoroacetylacetonato)-platinum(II) and -palladium(II) with tri-*o*-tolylphosphine<sup>9)</sup> also gave the *O*-bonded β-diketonate complexes. The present paper reports on the kinetic and equilibrium studies of the reaction between bis(trifluoroacetylacetonato)palladium(II) and tri-*o*-tolylphosphine.

### Experimental

**Materials.** Tri-*o*-tolylphosphine was recrystallized from ethanol and stored under nitrogen. Methanol and benzene were dried with Linde Molecular Sieves 3A and 4A, respectively, and distilled before use. Dichloromethane was stored over sodium carbonate, dried with Linde Molecular Sieve 4A, and distilled. Water contents of these solvents were determined with an MCI digital water microanalyzer CA-01 to be 3—4 × 10<sup>-3</sup> mol dm<sup>-3</sup> for methanol and 1—2 × 10<sup>-3</sup> mol dm<sup>-3</sup> for benzene and dichloromethane.

Bis(trifluoroacetylacetonato)palladium(II), Pd(tfac)<sub>2</sub>, was

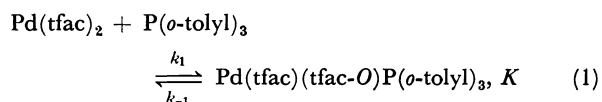
prepared according to Okeya *et al.*<sup>10)</sup> by reacting sodium hexachlorodipalladate(II) with trifluoroacetylacetone in methanol containing sodium carbonate. Found: C, 29.13; H, 1.94%. Calcd for C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>F<sub>6</sub>Pd: C, 29.11; H, 1.95%.

Trifluoroacetylacetonato(trifluoroacetylacetonato-*O*) (tri-*o*-tolylphosphine)palladium(II), Pd(tfac)(tfac-*O*)P(*o*-tolyl)<sub>3</sub>, was also prepared by the method of Okeya *et al.*<sup>9)</sup> A solution in benzene (20 cm<sup>3</sup>) of Pd(tfac)<sub>2</sub> (0.602 g, 1.46 mmol) and P(*o*-tolyl)<sub>3</sub> (0.456 g, 1.50 mmol) was stirred for 1 h and then concentrated to ca. 3 cm<sup>3</sup> by evaporation under reduced pressure. Petroleum ether (bp ca. 40 °C) was added dropwise to the concentrate to deposit an orange precipitate in an 85% yield, which was recrystallized from benzene-petroleum ether. Found: C, 52.07; H, 4.11%. Calcd for C<sub>31</sub>H<sub>29</sub>O<sub>4</sub>PF<sub>6</sub>Pd: C, 51.92; H, 4.08%.

**Measurements.** For the kinetic and equilibrium studies, absorbance at 380 nm was used which involves negligible contribution by uncoordinated P(*o*-tolyl)<sub>3</sub>. In benzene and dichloromethane, Pd(tfac)<sub>2</sub> (8—24 × 10<sup>-5</sup> mol dm<sup>-3</sup>) was allowed to react with excess P(*o*-tolyl)<sub>3</sub> (8—21 × 10<sup>-4</sup> mol dm<sup>-3</sup>) and the pseudo first order rate to attain the equilibrium was determined. In methanol, the equilibrium shifts further to right and a large excess of the phosphine (1—4 × 10<sup>-3</sup> mol dm<sup>-3</sup>) was used to measure the irreversible first order rate. The reverse reaction of Pd(tfac)(tfac-*O*)P(*o*-tolyl)<sub>3</sub> in benzene to produce Pd(tfac)<sub>2</sub> was also followed spectrophotometrically, and the first order rate constant was obtained by analyzing the initial stage of reaction. Spectral measurements were carried out with a Hitachi EPS-3T recording spectrophotometer and a Union stopped-flow rapid-scan spectrophotometer RA-1300.

### Results and Discussion

**Equilibria of the Reaction.** When a mixture of Pd(tfac)<sub>2</sub> and P(*o*-tolyl)<sub>3</sub> was stirred in benzene or dichloromethane for 24 h, the following reaction attained equilibrium. Concentrations of both the



palladium(II) complexes were calculated from their absorption spectra shown in Fig. 1. Values of the equilibrium constant *K* thus obtained in both solvents

\*\* In this paper, acac and tfac represent the acetylacetonate and trifluoroacetylacetonate anions, respectively, chelating a metal ion through two oxygen atoms, while acac-*O*, tfac-*O*, and acac-C<sup>3</sup> refer to the oxygen-bonded and central-carbon-bonded states, respectively.

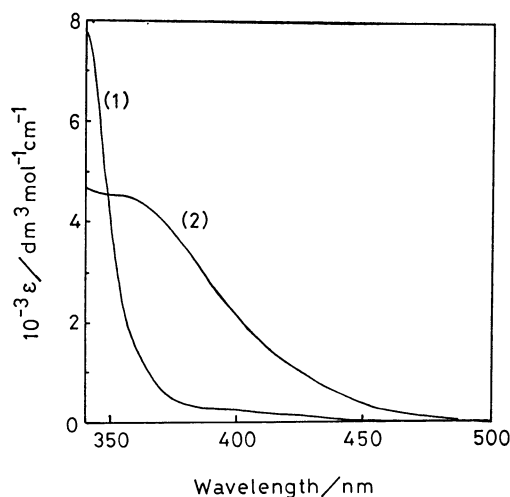


Fig. 1. Absorption spectra of Pd(tfac)<sub>2</sub> (curve 1) and Pd(tfac)(tfac-O)P(*o*-tolyl)<sub>3</sub> (curve 2) in benzene.

TABLE 1. EQUILIBRIUM CONSTANTS OF THE REACTION BETWEEN Pd(tfac)<sub>2</sub> AND P(*o*-tolyl)<sub>3</sub> (Eq. 1)

Solvent	Temp K	10 <sup>-3</sup> K dm <sup>3</sup> mol <sup>-1</sup>	ΔH° kJ mol <sup>-1</sup>	ΔS° J K <sup>-1</sup> mol <sup>-1</sup>
C <sub>6</sub> H <sub>6</sub>	318	0.680		
	308	0.958		
	298	1.38	-27.4 ± 0.2	-32.0 ± 0.6
	288	2.00		
CH <sub>2</sub> Cl <sub>2</sub>	298	4.35	-41.2 ± 2.1	-68.7 ± 7.1
	293	5.33		
	288	7.28		
	283	10.4		

at several temperatures are listed in Table 1. The plot of  $\ln K$  against  $1/T$  gave good straight lines (Fig. 2), from which the thermodynamic parameters were calculated and included in Table 1. Similar experiments in methanol were not successful for determining the equilibrium constant because of its too large value. Conversely, a methanol solution of Pd(tfac)(tfac-O)P(*o*-tolyl)<sub>3</sub> was kept in a 5-cm cell and degree of the phosphine dissociation was determined. In this way the

value of  $K$  in methanol at 25 °C was estimated to be larger than 10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup>.

As is seen in Table 1, reaction (1) is exothermic and the  $K$  value depends remarkably on the nature of solvent, increasing in the sequence, benzene < dichloromethane < methanol. The dangling carbonyl group of the unidentate tfac ligand might be stabilized by interaction with the hydrogen-bonding solvent. Even in the presence of a large excess of the phosphine, however, the product complex shows no sign of further substitution, whereas tricyclohexylphosphine (PCy<sub>3</sub>) reacts with Pd(tfac)<sub>2</sub> to afford not only Pd(tfac)(tfac-O)-PCy<sub>3</sub> but also [Pd(tfac)(PCy<sub>3</sub>)<sub>2</sub>](tfac).<sup>9)</sup> The large steric requirement of P(*o*-tolyl)<sub>3</sub> seems to make the bisphosphine complex thermodynamically unfavorable.

*Kinetics of the Reaction in Benzene and Dichloromethane.*

When Pd(tfac)<sub>2</sub> reacts with P(*o*-tolyl)<sub>3</sub> in benzene or dichloromethane, absorption spectrum of the solution changes with time, exhibiting an isobestic point at 348 nm, to reach a final spectrum corresponding to an equilibrium mixture of the two complexes. The plot of  $\ln(A_t - A_\infty)$  against time gave a straight line covering

TABLE 2. THE PSEUDO FIRST ORDER RATE CONSTANT FOR EQUILIBRIUM ATTAINMENT OF REACTION (1) AT 25 °C

Solvent	10 <sup>4</sup> [Complex] mol dm <sup>-3</sup>	10 <sup>8</sup> [Phosphine] mol dm <sup>-3</sup>	10 <sup>3</sup> k <sub>obsd</sub> s <sup>-1</sup>
C <sub>6</sub> H <sub>6</sub>	1.360	0.8140	0.262
		1.161	0.320
		1.380	0.363
		1.715	0.415
		2.105	0.485
CH <sub>2</sub> Cl <sub>2</sub>	2.176	0.8610	2.44
		1.151	3.12
	1.978	1.435	3.75
		1.628	4.20
		1.805	5.59
CH <sub>3</sub> OH	1.954	1.557	90.6
		1.984	116
		2.536	146
	2.356	2.602	148
		3.569	206

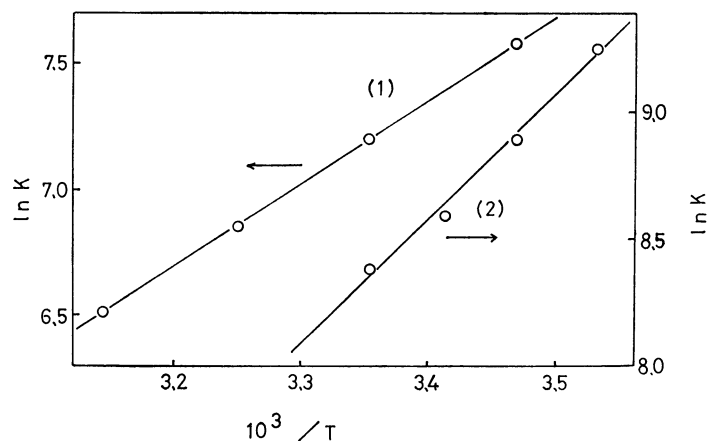


Fig. 2. Plot of  $\ln K$  for reaction (1) in benzene (line 1) and dichloromethane (line 2) against  $1/T$ .

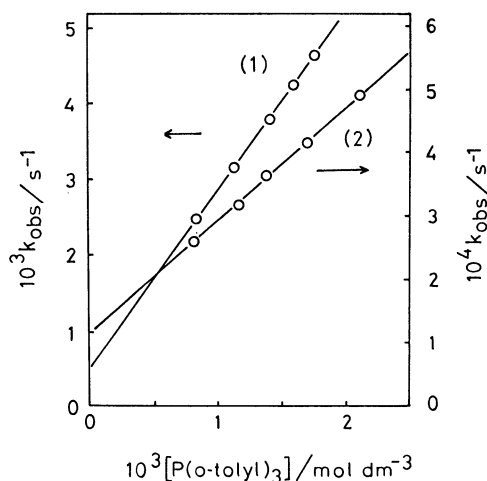


Fig. 3. Plot of the pseudo first order rate constant for the equilibrium attainment of reaction (1) in dichloromethane (line 1) and benzene (line 2) at 25 °C against the concentration of  $P(o\text{-tolyl})_3$ .

absorbances of the solution at 380 nm at time  $t$  and equilibrium, respectively. Thus the rate of reaction is expressed by Eq. 2 and the pseudo first order rate constant  $k_{\text{obsd}}$  increases with the concentration of  $P(o\text{-tolyl})_3$  (Table 2).

$$\text{rate} = k_{\text{obsd}}[\text{Pd}(\text{tfac})_2] \quad (2)$$

The plots of  $k_{\text{obsd}}$  against concentration of the phosphine give straight lines (Fig. 3) in line with the equation

$$k_{\text{obsd}} = k_1[P(o\text{-tolyl})_3] + k_{-1}. \quad (3)$$

TABLE 3. FORWARD AND REVERSE RATE CONSTANTS FOR REACTION (1) AT 25 °C

Solvent	$10^3 k_0/s^{-1}$	$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^4 k_{-1}/s^{-1}$
$\text{C}_6\text{H}_6$		$0.172 \pm 0.002$	$1.22 \pm 0.02$
$\text{CH}_2\text{Cl}_2$		$2.28 \pm 0.01$	$4.9 \pm 0.2$
$\text{CH}_3\text{OH}$	$2 \pm 1$	$56.6 \pm 0.6$	

more than three half-lives. Here  $A_t$  and  $A_\infty$  represent the forward and reverse rate constants,  $k_1$  and  $k_{-1}$  obtained from the slope and intercept of the straight line, respectively, are given in Table 3. Both the forward and the reverse reactions are faster in dichloromethane than in benzene. The values of  $K = k_1/k_{-1}$  calculated from these rate constants in benzene and dichloromethane are 1410 and 4650  $\text{dm}^3 \text{ mol}^{-1}$ , respectively, at 25 °C, showing satisfactory coincidence with those obtained from the equilibrium measurements (Table 1).

When a solution of  $\text{Pd}(\text{tfac})(\text{tfac-O})P(o\text{-tolyl})_3$  in benzene (*ca.*  $10^{-4} \text{ mol dm}^{-3}$ ) is left to stand, the phosphine molecule is expelled from the coordination sphere to produce  $\text{Pd}(\text{tfac})_2$ . The reaction attains equilibrium after decomposition of *ca.* 90% of the mixed-ligand complex (Fig. 4). Values of the first order rate constant  $k_{-1}$  obtained by analyzing the early stage of the reaction at a few temperatures are given in Table 4. The  $k_1$  values at each temperature were calculated by combining the value of  $k_{-1}$  with that of  $K$ . The values of  $k_1$  and  $k_{-1}$  at 25 °C thus obtained coincide with those

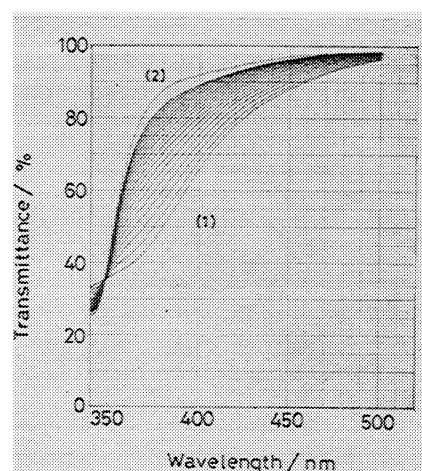


Fig. 4. Change with time of the absorption spectrum of a solution of  $\text{Pd}(\text{tfac})(\text{tfac-O})P(o\text{-tolyl})_3$  in benzene at 25 °C, curves 1 and 2 representing the spectra 5 min and 24 h after commencement of the reaction, respectively. The initial concentration of the starting complex was  $1.360 \times 10^{-4} \text{ mol dm}^{-3}$ .

TABLE 4. THE RATE CONSTANTS AND ACTIVATION PARAMETERS IN BENZENE

Temp K	$10 k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^4 k_{-1}/s^{-1}$
298	$1.71^{\text{a}}$	$1.24 \pm 0.01^{\text{b}}$
	$1.72 \pm 0.02^{\text{c}}$	$1.22 \pm 0.02^{\text{c}}$
308	$1.94^{\text{a}}$	$2.03 \pm 0.02^{\text{b}}$
318	$2.60^{\text{a}}$	$3.82 \pm 0.04^{\text{b}}$
$\Delta H^*/\text{kJ mol}^{-1}$	$14 \pm 3$	$42 \pm 3$
$\Delta S^*/\text{J K}^{-1} \text{ mol}^{-1}$	$-210 \pm 10$	$-180 \pm 10$

a) Calculated by combining the values of  $k_{-1}$  and  $K$  at each temperature. b) Determined directly by following the reverse reaction of (1). c) Determined by following the equilibrium attainment of (1).

determined under the reversible reaction conditions. The activation parameters related to  $k_1$  and  $k_{-1}$  in benzene were obtained from the Eyring plot and are included in Table 4. The data used for calculations are insufficient to allow detailed discussion, but the small values of  $\Delta H^*$  associated with  $k_1$  accords with the fast rate of reaction (1),  $\Delta S^*$  being largely negative as is expected for the associative mechanism. Even  $\Delta S^*$  for the reverse  $k_{-1}$  reaction is largely negative and might be related with the intramolecular nucleophilic attack of the dangling trifluoroacetyl group on the central metal atom. The differences between the kinetic parameters,  $\Delta(\Delta H^*)$  and  $\Delta(\Delta S^*)$ , for the forward and reverse processes of reaction (1) coincide with  $\Delta H^\circ$  and  $\Delta S^\circ$  determined by equilibrium studies.

*Kinetics of the Reaction in Methanol.* The reaction in methanol was carried out under the irreversible pseudo first order conditions employing a large excess of  $P(o\text{-tolyl})_3$ . The plot of  $k_{\text{obsd}}$  thus obtained (Table 2) against the concentration of  $P(o\text{-tolyl})_3$  gives a straight line (Fig. 5). The intercept of the straight line can not be the reverse rate contrary to the case for the reaction in benzene and dichloromethane (Fig. 3), since the

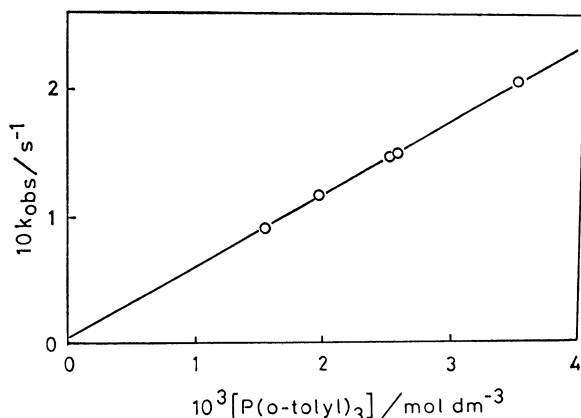


Fig. 5. Plot of the pseudo first order rate constant for the forward reaction of (1) in methanol at 25 °C against the concentration of P(*o*-tolyl)<sub>3</sub>.

equilibrium constant in methanol was estimated to be greater than  $10^9 \text{ dm}^3 \text{ mol}^{-1}$ . The rate thus follows the two term rate law:

$$k_{\text{obsd}} = k_0 + k_1[P(o\text{-tolyl})_3]. \quad (4)$$

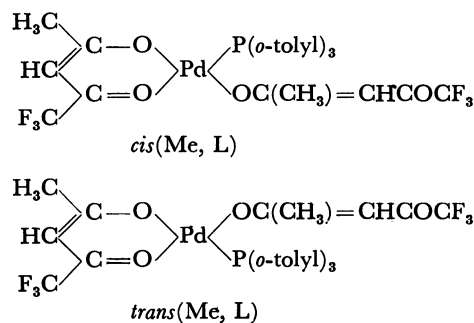
This type of rate equation is widely applicable to the ligand substitution reactions of square planar complexes,<sup>11</sup> the first term being attributed to the nucleophilic attack of a solvent molecule on the complex. In the case of Fig. 3, the intercept was entirely ascribed to the reverse rate, giving a consistent value of equilibrium constant. Thus the solvent path is not involved in the forward reaction in benzene and dichloromethane, but contributes a little to the reaction in methanol which has higher coordination ability.

The rate constant  $k_1$  for the reagent path also depends remarkably on the nature of solvent, decreasing in the sequence  $\text{CH}_3\text{OH} \gg \text{CH}_2\text{Cl}_2 > \text{C}_6\text{H}_6$  (Table 3). The ratio of rates in methanol and benzene, 330 : 1, is larger than that (180 : 1) observed for the reaction of Pd(acac)<sub>2</sub> with dipropylamine.<sup>11</sup> Such a solvent effect might be related to the difference in hydrogen-bonding ability. A solvent molecule might interact with a carbonyl group of the coordinated tfac anion, enhancing the one bond cleavage of the chelated ligand. Of the three kinds of solvents, methanol has the highest tendency of hydrogen bonding and dichloromethane possesses weak hydrogen donating ability.<sup>12</sup>

The change of spectrum during the course of reaction (1) in each solvent shows a distinct isosbestic point, indicating that the five-coordinate intermediate is not accumulated enough to be detected spectrophotometrically. Bis(hexafluoroacetylacetonato)palladium(II) reacts with P(*o*-tolyl)<sub>3</sub> to afford Pd(hfac)<sub>2</sub>P(*o*-tolyl)<sub>3</sub>, which was confirmed by X-ray analysis to have a squarepyramid structure with the phosphine at a basal position.<sup>13</sup> On the other hand, Pd(acac)<sub>2</sub> does not

react with P(*o*-tolyl)<sub>3</sub> at all.<sup>9</sup> The three related Pd( $\beta$ -dik)<sub>2</sub> complexes show substantially different tendency of reaction with P(*o*-tolyl)<sub>3</sub>.

The starting complex Pd(tfac)<sub>2</sub> was reported to have the *trans* configuration in solid but exist as a mixture of *cis* and *trans* (1 : 3) in C<sub>6</sub>D<sub>6</sub>.<sup>10</sup> As to the structure of the reaction product, there exist the following two possibilities and the <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> showed that the isomer ratio *cis*(Me, L)/*trans*(Me, L) in equilibrium is 1/5.<sup>9</sup>



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