

Reactions of Tris(tribenzylidene acetylacetonate)—— tripalladium with Triarylpanicogens

Jugo KOKETSU* and Yoshio ISHII*

(Received March 26, 1980)

The complex tris(tribenzylidene acetylacetonate)tripalladium, $\text{Pd}_3(\text{TBAAC})_3$, reacts with triarylpanicogens (Ar_3E , $\text{E}=\text{P}$, As and Sb) to give $\text{Pd}(\text{Ar}_3\text{E})_4$ and free olefinic ligand. The rate of the exchange reaction is studied by monitoring the decrease in the amount of the complex under the condition which ensures the pseudo-first order reaction. The pseudo-first order rate constants (k_{obs}) vary with the ligand concentration $[\text{Ar}_3\text{E}]$. A linear plot of $(k_{\text{obs}}/[\text{Ar}_3\text{E}]-k_a)^{-1}$ vs. ligand concentrations was found by assuming the steady-state approximation, and this indicates a reaction mechanism having two paths, one is associative with the ligand (rate constant; k_a) and the other is a dissociative path. The rate constants of the associative path (k_a) vary with Ph_3E in the order $\text{Ph}_3\text{Sb} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$. This order implies that the π -acceptability of the panicogen ligands plays an important role in the reaction of $\text{Pd}(0)$ complex. Exactly the same treatment of the rate measurement was applied to the reaction between tetraphenylcyclobutadiene palladium chloride dimer, $(\text{PdCl}_2(\text{Ph}_4\text{C}_4))_2$, and triarylpanicogens, and the reaction mechanism was confirmed to be the same as in the case of the $\text{Pd}(0)$ complex. The reactivity order of the panicogen ligands in an associative path of the reaction is found to be $\text{Ph}_3\text{P} > \text{Ph}_3\text{As} > \text{Ph}_3\text{Sb}$. Therefore, it seems that the σ -donor ability of the panicogen ligand is important in the reaction of $\text{Pd}(\text{II})$ complex.

1. Introduction

The complex, $\text{Pd}_3(\text{TBAAC})_3$, was prepared by Ishii's group¹⁾ and found to be an interesting zerovalent Pd complex containing only olefinic ligands. This complex is stable in air and useful as a starting material for the preparation of various $\text{Pd}(0)$ complexes. Concerning the reaction of this complex, oxidative addition reaction, and complex formation reactions with maleic anhydride, dimethylacetylene dicarboxylate and *p*-quinone have been investigated.¹⁾ The ligand exchange reaction of the complex with panicogen ligands, however, has not yet been investigated except for the reaction with triphenylphosphine.¹⁾ The kinetic study of the ligand exchange reaction of

*Department of Industrial Chemistry.

$\text{Pd}_2(\text{TBA})_2$ with triarylpcnicogen will give useful information about the reactivity of the $\text{Pd}(0)$ complex and of the pcnicogen ligands too. The relative σ -donor and π -acceptor properties of the pcnicogen ligands vary depending on the class of the metal and on the metal oxidation state. Generally speaking, metals in oxidation state II or higher form essentially pure σ -bond with the pcnicogen ligands, and metals in oxidation state 0 or lower form σ with π -bond with the pcnicogen ligands.²⁹ Therefore, it is expected that in the reaction of $\text{Pd}_2(\text{TBA})_2$ with pcnicogen ligand, the π -acceptability of the pcnicogen atoms affect the exchange rate in a striking manner. In order to compare the effect of the oxidation state of the metal ion, we chose tetraphenylcyclobutadiene palladium dimer, $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$, as an example of $\text{Pd}(\text{II})$ complex. This complex is known to react with triarylpcnicogens to give bis (triarylpcnicogen)palladium dichloride.³⁰

2. Experimental

Materials. Tris(tribenzylidene acetylacetone)tripalladium,³¹ and tetraphenylcyclobutadiene palladium dimer³² were prepared as in the literatures. Triarylpcnicogens were obtained by the reaction of the corresponding arylmagnesium bromide with trichloropcnicogens. All the solvents were dried over calcium hydride and distilled before use.

Kinetic procedure. The rate of the ligand exchange reactions were measured spectrophotometrically. A Hitachi 200-10 spectrophotometer was used to follow the change in absorbance with time. In a typical experiment, 3.0 ml of the complex solution in desired medium was placed in a cell of 1-cm path length in a thermostatted cell compartment and was allowed to thermally equilibrate (ca. 5 min.). The reaction was started by adding a calculated amount (at least 10 fold excess) of the ligand solution by using a microsyringe. Immediately after injection of the ligand solution, the reaction solution was mixed thoroughly by pumping the solution with 2 ml syringe. Absorbance changes in characteristic absorption of these complexes with time were monitored till at least 5 half-lives. $\text{Pd}_2(\text{TBA})_2$ and $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ have their characteristic absorptions at 530 nm ($\epsilon=15,000$) and 395 nm ($\epsilon=9,000$), respectively. Typically, the concentration of the complex was 2.0×10^{-5} mol/l, and the ligand concentrations were varied from 0.5×10^{-3} mol/l to 6.0×10^{-3} mol/l. From the absorbance changes, good linear plots of $\ln(A_t - A_\infty)$ against time were obtained and the pseudo-first order rate constants (k_{obs}) were calculated from the slope of these lines, where A_t is the absorbance at time t and A_∞ is the absorbance at 5 half-lives. The reaction of $\text{Pd}_2(\text{TBA})_2$ with triphenylstibine in benzene at higher temperatures than 8°C was too fast to study kinetically by this method. The poor solubility of $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ in most organic solvents including benzene forced us to study the reaction in methylene chloride only.

Identification of Reaction Products. The complex $\text{Pd}_2(\text{TBA})_2$ (0.506 g, 0.33 mmole) and Ph_3P (1.50 g, 11.5 mmole) were dissolved in diethylether and allowed to react for 24 hrs at room temperature, and the complex $\text{Pd}(\text{Ph}_3\text{P})_4$ was obtained

almost quantitatively (96%), and further purified by recrystallization from methylene chloride. The other $\text{Pd}(\text{Ar}_3\text{E})_4$ complexes were prepared similarly. The similar reaction of $[\text{PdCl}_2(\text{Ph}_3\text{C}_4)]_2$ with triarylpnicogens in methylene chloride gave $(\text{Ar}_3\text{E})_2\text{PdCl}_2$ complexes in quantitative yields. The elemental analyses and some physical properties of $\text{Pd}(\text{Ar}_3\text{E})_4$ and $(\text{Ar}_3\text{E})_2\text{PdCl}_2$ are shown in Table 1.

Table 1. Elemental analyses and physical properties of $\text{Pd}(\text{L})_4$ and $\text{PdCl}_2(\text{L})_2$

	L	Color	m.p.(°C)	CH-Analysis	
				C% (Calc.)	H% (Calc.)
$\text{Pd}(\text{L})_4$	Ph_3P	Yellow	105~106	74.6(75.84)	5.25(5.23)
	Ph_3As	Yellow	300 ^{a)}	62.2(64.94)	4.85(4.54)
	Ph_3Sb	Green	300 ^{a)}	54.3(56.94)	3.14(3.98)
	$(p\text{-ClC}_6\text{H}_4)_3\text{P}$	Orange	95~98	55.6(55.12)	3.26(3.08)
	$(p\text{-ClC}_6\text{H}_4)_3\text{As}$	Yellow	175~177	49.9(49.57)	2.52(2.77)
	$(p\text{-ClC}_6\text{H}_4)_3\text{Sb}$	Yellow	245~251	44.6(44.76)	2.85(2.50)
	$(p\text{-MeC}_6\text{H}_4)_3\text{P}$	Orange	248~251	76.3(76.21)	6.24(6.40)
	$(p\text{-MeC}_6\text{H}_4)_3\text{As}$	Yellow	143~146	67.3(67.20)	5.63(5.65)
	$(p\text{-MeC}_6\text{H}_4)_3\text{Sb}$	Brown	206~209	59.5(59.81)	5.42(5.02)
$\text{PdCl}_2(\text{L})_2$	Ph_3P	Yellow	293~294	61.4(61.61)	4.52(4.31)
	Ph_3As	Yellow	240 ^{a)}	54.5(54.75)	3.78(3.83)
	Ph_3Sb	Yellow	176 ^{a)}	48.7(48.94)	3.30(3.42)

a) Dec. point.

3. Results and discussion

The pseudo-first order rate constants (k_{obs}) of the reaction of $\text{Pd}_3(\text{TBA A})_3$ with Ph_3P at 15.0 and 22.0°C in benzene are shown in Table 2. The relation of k_{obs} with the concentration of Ph_3P (L) is shown in Fig. 1. The results shown in Fig. 1 demonstrate that there are two reaction paths, one is associative with the ligands and the other is a

Table 2. Pseudo-first order rate constants for the reaction of $\text{Pd}_3(\text{TBA A})_3$ with Ph_3P at 15.0 and 22.0°C in benzene

$(\text{L}) \times 10^3$	$k_{obs} \times 10^3 (\text{sec.}^{-1})$	
	at 15.0°C	at 22.0°C
0.487	9.74 ± 0.07	26.0 ± 0.1
1.216	18.33 ± 0.06	40.3 ± 0.9
2.424	30.6 ± 0.1	65.9 ± 0.8
3.684	39.4 ± 0.2	82.7 ± 0.8
4.816	46.8 ± 0.5	98.9 ± 0.9
6.000	54.6 ± 0.5	115.0 ± 1.0

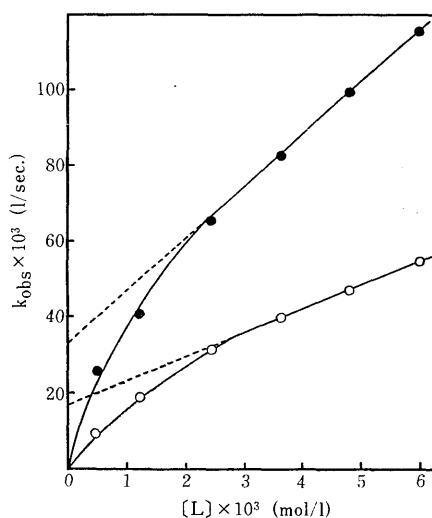
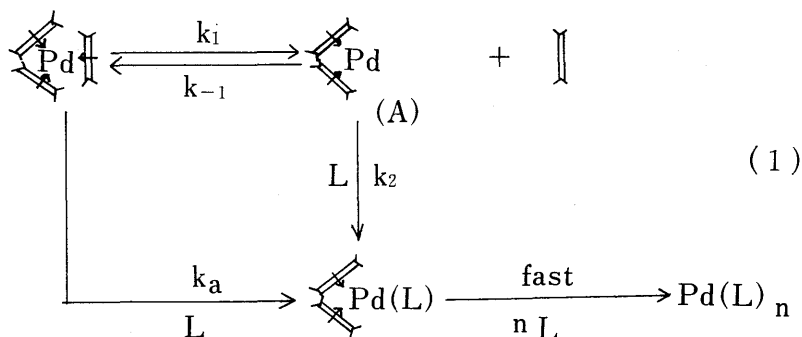


Fig. 1. Variation of the pseudo-first order rate constants with the ligand concentration in benzene at 15.0 (○) and 22.0°C (●).

dissociative path involving initial cleavage of Pd-olefin bond as shown in Eq. 1.



By assuming the steady state approximation to the intermediate A, the rate law is obtained (Eq. 2).

$$v = \frac{k_1 k_2 [L] [\text{complex}]}{k_{-1} + k_2 [L]} + k_a [L] [\text{complex}] \quad (2)$$

thus,

$$k_{obs} = \frac{k_1 k_2 [L]}{k_{-1} + k_2 [L]} + k_a [L] \quad (3)$$

In the case of the ligand concentration being very high, $k_2 [L] \gg k_{-1}$, $k_{obs} = k_1 + k [L]$ was obtained. The gradient part of the plot in Fig. 1 gives the rate constant of the associative path (k_a), while the intercept of this extrapolated line gives the rate constant of the dissociative path (k_1). Equation 3 can be rearranged to the Eq. 4.

$$(k_{obs}/[L] - k_a)^{-1} = k_{-1}/k_1 k_2 + [L]/k_1 \quad (4)$$

The linear correlation of $(k_{obs}/[L] - k_a)^{-1}$ with $[L]$ shown in Fig. 2 confirms the validity of the proposed mechanism. From the intercept of the plots in Fig. 1, k_1 was obtained and proved to be the same value within experimental error as that obtained from the slope of the line in Fig. 2. The same treatment of the pseudo-first order rate constants can be applied to the reactions between $\text{Pd}_2(\text{TBA})_2$ and the other triarylpnicogens. The rate constants, k_a and k_1 at a variety of temperatures in several solvents are tabulated in Table 3.

Exactly the same treatment of the rate measurement was applied to the reaction of $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ with pnicogen ligands, and the similar competition reaction mechanism was confirmed. In this case the reaction was performed in methylene chloride because of poor solubility of this complex in benzene. The reaction of phosphine ligands with this complex is too fast to follow by the method used in this experiment. The results are shown in Table 4. The

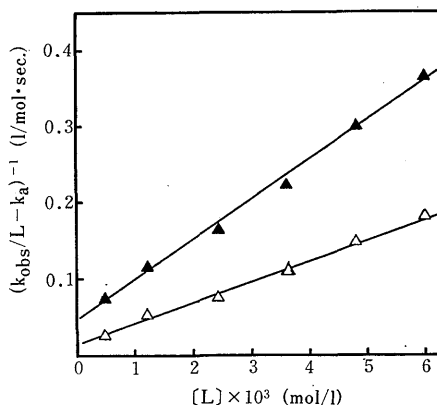


Fig. 2. Plots of $(k_{obs}/L - k_a)^{-1}$ against the ligand concentration in benzene at 15.0 (△) and 22.0°C (▲).

Table 3. Kinetic data for reaction of $\text{Pd}_3(\text{TBA})_3$ with triarylpnicogen in benzene

Ligand	Temp (°C)	k_a (mol/l. sec.)	k_1 (1/sec.)
Ph_3P	8.0	3.22 ± 0.07	6.54 ± 0.05
	12.0	4.53 ± 0.06	10.32 ± 0.08
	15.0	6.36 ± 0.08	17.04 ± 0.08
	19.0	9.17 ± 0.08	27.18 ± 0.09
	22.0	13.7 ± 0.1	32.9 ± 0.1
	15.0 ^{a)}	3.52 ± 0.07	32.2 ± 0.1
	15.0 ^{b)}	3.32 ± 0.07	40.1 ± 0.1
Ph_3As	8.0	3.29 ± 0.04	6.91 ± 0.08
	12.0	4.86 ± 0.05	10.6 ± 0.08
	15.0	6.86 ± 0.08	21.4 ± 0.06
	19.0	10.1 ± 0.1	28.8 ± 0.1
	22.0	13.7 ± 0.1	39.2 ± 0.1
	15.0 ^{a)}	3.92 ± 0.07	32.9 ± 0.1
	15.0 ^{b)}	3.41 ± 0.07	39.6 ± 0.1
Ph_3Sb	8.0	34.5 ± 0.1	6.91 ± 0.09
$(p\text{-ClC}_6\text{H}_4)_3\text{P}$	15.0	6.79 ± 0.09	27.6 ± 0.2
$(p\text{-MeC}_6\text{H}_4)_3\text{P}$	15.0	3.96 ± 0.04	20.7 ± 0.1
$(p\text{-ClC}_6\text{H}_4)_3\text{As}$	15.0	7.78 ± 0.09	25.6 ± 0.1
$(p\text{-MeC}_6\text{H}_4)_3\text{As}$	15.0	5.02 ± 0.07	20.7 ± 0.1
$(p\text{-ClC}_6\text{H}_4)_3\text{Sb}$	8.0	35.7 ± 0.1	6.91 ± 0.08
$(p\text{-MeC}_6\text{H}_4)_3\text{Sb}$	8.0	32.9 ± 0.1	6.91 ± 0.08

a) In 1,1,1-trichloroethane. b) In 1,2-dichloroethane.

Table 4. Kinetic data for the reaction of $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ with triarylpnicogen in dichloromethane

Ligand	Temp (°C)	k_a (mol/l. sec.)	k_1 (1/sec.)
Ph_3P		Too fast to follow	
Ph_3As	10.0	44.7 ± 0.2	3.50 ± 0.07
	12.0	47.0 ± 0.3	4.4 ± 0.1
	17.2	54.1 ± 0.2	8.1 ± 0.1
	19.5	58.5 ± 0.2	9.6 ± 0.2
	22.2	61.7 ± 0.2	12.0 ± 0.2
$(p\text{-ClC}_6\text{H}_4)_3\text{As}$	18.0	3.57 ± 0.05	11.5 ± 0.1
$(p\text{-MeC}_6\text{H}_4)_3\text{As}$	18.0	61.5 ± 0.1	10.9 ± 0.1
Ph_3Sb	18.0	0.92 ± 0.01	11.3 ± 0.1
	22.0	1.13 ± 0.01	12.6 ± 0.1
	26.5	1.38 ± 0.1	20.0 ± 0.2
	30.0	1.43 ± 0.1	28.8 ± 0.2
$(p\text{-ClC}_6\text{H}_4)_3\text{Sb}$	18.0	0.46 ± 0.01	11.5 ± 0.1
$(p\text{-MeC}_6\text{H}_4)_3\text{Sb}$	18.0	1.38 ± 0.02	12.5 ± 0.1

same mechanism mentioned above has been proposed for the reaction of η^4 -heterodieneiron tricarbonyl compounds with pnictogen ligands⁴⁾ and also for the reaction of η^4 -enoneiron tricarbonyl 1,3,5-cycloheptatriene with pnictogen ligands.⁵⁾ In the reac-

tions of $\text{Pd}_3(\text{TBA})_3$ and $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ with pnictogen ligands, the experimental results can be explained completely by this mechanism. The existence of the intermediate A is not proved, but the observation of the resonance from free ligand in $\text{Pd}_3(\text{TBA})_3$ NMR spectra¹¹ implies the presence of the intermediate A. The nature of the ligands has no effect on the dissociative process, therefore, the rate constants, k_1 's, are almost constant at each temperature. Because of the non-ionic property of this exchange reaction, it was expected that the polarity of the solvent would not greatly influence the rates. However, the rate constants k_1 's increase with increasing polarity of the solvent, and this fact presumably means that the unoccupied site on the Pd metal will be occupied by the solvent, and this interaction of Pd metal with the solvent will increase with increasing polarity of the solvent used and accelerate the dissociation step. Concerning the reaction rate of the associative process in this reaction, the reactivity order of the triphenylpnictogens was found to be $\text{Ph}_3\text{Sb} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$. This is the reverse order of the nucleophilicity and basicity of the triphenylpnictogens.^{6, 7, 9} In each pnictogen ligand, electron withdrawal substituents accelerate the associative process. It has been observed that the electron density on the manganese atom in $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_2\text{Ph}_3\text{E}$, decrease in the order $\text{Ph}_3\text{Sb} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$.^{9, 10} This fact indicates the large pnictogen atom accepts strongly the electron density from manganese atom. And the π -parameter determined by Graham using the carbonyl stretching force constants in $\text{Ph}_3\text{EMn}(\text{CO})_5$ and $\text{Ph}_3\text{EMo}(\text{CO})_5$ also falls in the order $\text{Ph}_3\text{Sb} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$.¹¹ On the contrary, in an associative path of the reaction between $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ and pnictogen ligands, the reactivity order is completely inversed compared with the case of $\text{Pd}_3(\text{TBA})_3$. So it seems that in the reaction of $\text{Pd}(\text{II})$ complex, the σ -donor ability of the pnictogen ligands is important, and also an electron withdrawal substituent retards an associative reaction. In the reaction of triphenylpnictogens with $\text{Fe}(0)$ complex, such as $\text{Fe}(\text{CO})_5(\eta^4\text{-PhCH=CHCH=NAr})$,⁴ the reactivity order has been reported to be $\text{Ph}_3\text{P} > \text{Ph}_3\text{As} \approx \text{Ph}_3\text{Sb}$, and it was concluded that the nucleophilicity of the ligands affects the associative step in the reaction. But in the case of the reaction of $\text{Pd}(0)$ complex, the electron acceptability, i.e. π -acceptability of the pnictogen atom plays an important role in determining the rate of the associative step. The activation parameters are shown in Table 5. The activation energies are high for the dissociation process and the large log A values also are indicative of the one molecular dissociative process. For the associa-

Table 5. Arrhenius parameters of the dissociative and associative steps

Complex	Ligand	k_a		k_1	
		ΔE_a (Kcal/mol)	log A	ΔE_a (Kcal/mol)	log A
$\text{Pd}_3(\text{TBA})_3$ a)	Ph_3P	16.1 ± 0.9	12.7 ± 0.7	21.0 ± 1.0	17.1 ± 0.8
	Ph_3As	16.8 ± 0.6	13.2 ± 0.5		
$[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ b)	Ph_3As	4.5 ± 0.2	4.8 ± 0.2	17.3 ± 0.9	13.9 ± 0.9
	Ph_3Sb	5.9 ± 0.7	4.1 ± 0.5		

a) In benzene. b) In dichloromethane.

tive step of the reaction of $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$, small $\log A$ values indicate bi-molecular association step. The large $\log A$ values for the associative step of the reaction of $\text{Pd}_3(\text{TBA})_3$ seems to be unusual. But the $\text{Pd}_3(\text{TBA})_3$ is trinuclei complex and the exchange reaction leads to the formation of mononuclear complex $\text{Pd}(\text{Ph}_3\text{E})_4$, there must be a large increase in the total entropy of the system. This large entropy increase might effect the activation entropy of the associative step. The solvent effect on the associative step of the reaction of $\text{Pd}_3(\text{TBA})_3$ is a reversed order compared to the case of the dissociative step. This fact indicates that desolvation from $\text{Pd}_3(\text{TBA})_3$ participates in the rate determining step of the associative step. Unfortunately, the poor solubility of $[\text{PdCl}_2(\text{Ph}_4\text{C}_4)]_2$ in most organic solvents prevents us from studying the solvent effect on the reaction with pnictogen ligands.

References

- 1) Y. Ishii, S. Hasegawa, S. Kimura, and K. Itoh, *J. Organomet. Chem.*, **73**, 411 (1974).
- 2) J. Emsley, and D. Hall, "The Chemistry of Phosphorus," Harper & Row Publisher, London (1976), p.177.
- 3) P. M. Maitlis, D. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965).
- 4) G. Cardaci, and G. Bellachioma, *Inorg. Chem.*, **16**, 3099 (1977).
- 5) G. Bellachioma, and G. Cardaci, *J. Chem. Soc., Dalton Trans.*, **1977**, 2181.
- 6) O. W. Kolling and F. A. Mawdsley, *Inorg. Chem.*, **9**, 408 (1970).
- 7) G. E. Parris, and F. E. Brickman, *J. Org. Chem.*, **27**, 3801 (1975).
- 8) R. G. Pearson, and H. Sobel, *J. Am. Chem. Soc.*, **90**, 319 (1968).
- 9) C. Barbeau, *Can. J. Chem.*, **45**, 161 (1967).
- 10) W. Storchweier, *Z. Naturforsch., Teil B*, **19**, 319 (1968).
- 11) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).