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Kinetics and Mechanism of the Reactions of Bis(acetylacetonato)-palladium(II) with Alkylamines

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The reactions of bis(acetylacetonato)palladium(II), Pd(acac)$_2$, with alkylamines (L) such as butyl-, cyclohexyl-, diethyl-, and dipropylamines in methanol to afford [Pd(acac)L$_2$](acac) obey the usual two-term rate law, rate$=(k_0+k_1[\mathrm{L}])[\mathrm{Pd(acac)_2}]$. On the other hand, the rate of reaction of Pd(acac)$_2$ with diethylamine in THF and benzene is expressed by rate$=(k_1+k_2[\mathrm{L}])[\mathrm{L}][\mathrm{Pd(acac)_2}]$. A mechanism is proposed which presumes the hydrogen-bonding interaction of Pd(acac)$_2$ with methanol and amine. Intermediacy of Pd(acac)(acac-C^3)L in these reactions was denied on the basis of the kinetic studies, and the carbon-bonded complex was concluded to be produced *via* [Pd(acac)L$_2$](acac). The equilibrium constants for the reactions, Pd(acac)$_2$+2Et$_2$NH$\rightleftarrows$[Pd(acac)(Et$_2$NH)$_2$](acac) and Pd(acac)(acac-C^3)(Et$_2$NH)+Et$_2$NH$\rightleftarrows$[Pd(acac)(Et$_2$NH)$_2$](acac) were determined in dichloromethane and methanol.

The central-carbon-bonded complexes of acetylacetone and other β-dicarbonyl compounds have long been known for platinum, mercury, and other rather soft metal ions.[1] Strange to say, the palladium(II) complex of this sort had not been reported before 1971, when Baba *et al.* found that bis(acetylacetonato)palladium(II), Pd(acac)$_2$,** reacts with bases such as triphenylphosphine, pyridine, and diethylamine to convert one of the chelating ligands into the central-carbon-bonded state.[2] The molecular structure of Pd(acac)(acac-C^3)PPh$_3$ was confirmed by X-ray analysis.[3] Similar reactions have been successfully carried out with Pt(acac)$_2$,[4] AuMe$_2$(acac),[5] and Pd(etac)$_2$ (etac=O,O'-chelated monoanion of ethyl acetoacetate)[6] to obtain the central-carbon-bonded complexes of β-dicarbonyl compounds.

When bis(β-diketonato)palladium(II) was reacted with excess nitrogen bases (L), *e.g.* in neat liquid, the β-diketonate anion, (β-dik), such as acetylacetonate, trifluoroacetylacetonate, and hexafluoroacetylacetonate was expelled from the coordination sphere to produce [Pd(β-dik)L$_2$](β-dik) or [PdL$_4$](β-dik)$_2$ depending on the nature of L.[7] In order to clarify whether or not the chelated β-diketonate ligand dissociates *via* the central-carbon-bonded state, kinetic and equilibrium studies on the reactions of Pd(acac)$_2$ with several alkylamines have been performed by the spectrophotometric method.

Experimental

Materials. Bis(acetylacetonato)palladium(II) was prepared according to the literature[8] and recrystallized twice from benzene. Found: C, 39.52; H, 4.64%. Calcd for $C_{10}H_{14}O_4Pd$: C, 39.46; H, 4.59%. All of the amines used in the following preparation of complexes were dried with sodium sulfate and distilled before use. Methanol and benzene were dried with Linde Molecular Sieves 3A and 4A, respectively, and distilled. Tetrahydrofuran (THF) was kept standing with lithium aluminium hydride for several days prior to distillation. The distillate was dried with Linde Molecular Sieve 3A and redistilled. Dichloromethane was treated with potassium carbonate, dried with Linde Molecular Sieve 4A and distilled. Water contents of organic solvents were checked with an MCI digital water microanalyzer CA-Ol to be 1—2$\times10^{-3}$ mol dm^{-3} in benzene and 3—4$\times10^{-3}$ mol dm^{-3} in other solvents employed.

Acetylacetonatobis(diethylamine) palladium (II) acetylacetonate, [Pd(acac)(Et$_2$NH)$_2$] (acac), was prepared by the method reported by Okeya *et al.*[7]; Pd(acac)$_2$ (0.400 g) was dissolved in hot diethylamine (5 ml) and the solution was cooled to −20 °C to deposit the product in a 22% yield. Found: C, 47.86; H, 8.08; N, 6.02%. Calcd for $C_{18}H_{36}O_4N_2Pd$: C, 47.97; H, 8.05; N, 6.21%.

Acetylacetonato(acetylacetonato-C^3)(diethylamine) palladium(II), Pd(acac)(acac-C^3)(Et$_2$NH), was prepared according to Baba *et al.*[2] and recrystallized from dichloromethane–petroleum ether (bp *ca.* 50 °C). Found: C, 47.11, H, 5.07; N, 3.71%. Calcd for $C_{14}H_{25}O_4NPd$: C, 47.11; H, 5.00; N, 3.65%.

Acetylacetonatobis(cyclohexylamine) palladium(II) acetylacetonate, [Pd(acac)(cyhxNH$_2$)$_2$](acac), was obtained as pale yellow fuzzy needles in a 68% yield on addition of diethyl ether to a reaction mixture of Pd(acac)$_2$ (0.200 g) with cyclohexylamine (2 ml) in dichloromethane (10 ml) after 30 min stirring at room temperature, and recrystallized from dichloromethane–diethyl ether. Found: C, 52.74; H, 8.15; N, 5.80%. Calcd for $C_{22}H_{40}O_4N_2Pd$: C, 52.57; H, 8.02; N, 5.57%.

Preparation and recrystallization of these mixed-ligand complexes must be carried out quickly to obtain pure substances. Prolonged handling in solution induces side reactions. Acetylacetonatobis(butylamine)palladium(II) and acetylacetonatobis(dipropylamine) palladium(II) acetylacetonates were also prepared but did not give satisfactory analyses, probably owing to contamination with by-products containing the carbon-bonded acetylacetonate ligand.

Kinetic and Equilibrium Measurements. Absorption spectra were measured with a Hitachi EPS-3T recording spectrophotometer. The reactions of Pd(acac)$_2$ with alkylamines were followed spectrophotometrically at 330 nm, the absorption maximum of the startimg complex. A large excess (50—10000 times) of amine was employd against Pd(acac)$_2$ (6—50$\times10^{-5}$ mol dm^{-3}) to attain the pseudo first order condition. The reaction of Pd(acac)(acac-C^3)(Et$_2$NH) with diethylamine was also followed spectrophotometrically at 295 nm and the pseudo first order condition was fulfilled by using 5000—15000 times amine against the complex (8—11$\times10^{-5}$ mol dm^{-3}).

** In this paper, acac represents an acetylacetonate anion chelated to a metal ion through two oxygen atoms, and acac-C^3 and acac-O stand for acetylacetonate anions bonded as a unidentate to a metal ion through the central carbon and an oxygen, respectively.

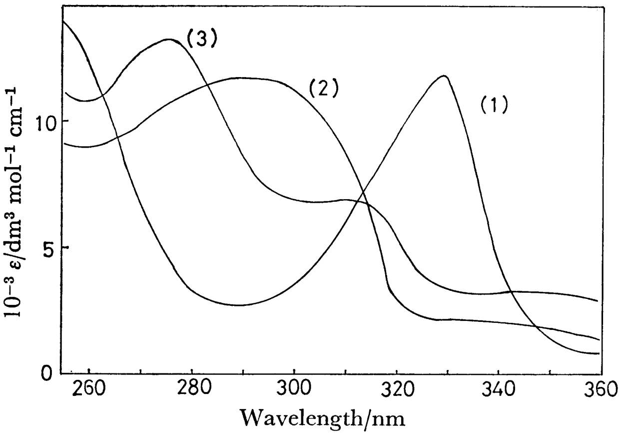

Fig. 1. Absorption spectra of $Pd(acac)_2$ (1), $[Pd(acac)(Et_2NH)_2]$ (acac) (2), and Pd (acac) (acac-C^3) (Et_2NH) (3) in dichloromethane.

In the experiments to determine the equilibria in dichloromethane, solutions containing $[Pd(acac)(Et_2NH)_2]$ (acac) (1—4×10^{-2} mol dm^{-3}) and diethylamine (0—4×10^{-2} mol dm^{-3}) were kept at 25 °C for 24 h. Absorption spectra were measured immediately after dilution of the equilibrated solution to *ca.* 10^{-4} mol dm^{-3}, and absorbances at 290, 300, 320, and 330 nm were used to determine concentrations of three complexes, $Pd(acac)_2$, Pd(acac)(acac-C^3)(Et_2NH), and $[Pd(acac)(Et_2NH)_2]$(acac) on the basis of their spectra displayed in Fig. 1. Equilibria in methanol were attained by mixing solutions of $Pd(acac)_2$ (2—8×10^{-5} mol dm^{-3}) and diethylamine (2—15×10^{-4} mol dm^{-3}) and keeping the mixture at 25 °C for 24 h. Absorbances at 330 nm were utilized to obtain the equilibrium concentrations of Pd $(acac)_2$ and $[Pd(acac)(Et_2NH)_2]$ (acac).

Results

Kinetics of the Reactions of $Pd(acac)_2$ *with Alkylamines.* Figure 2 shows, as an example, the change of absorption

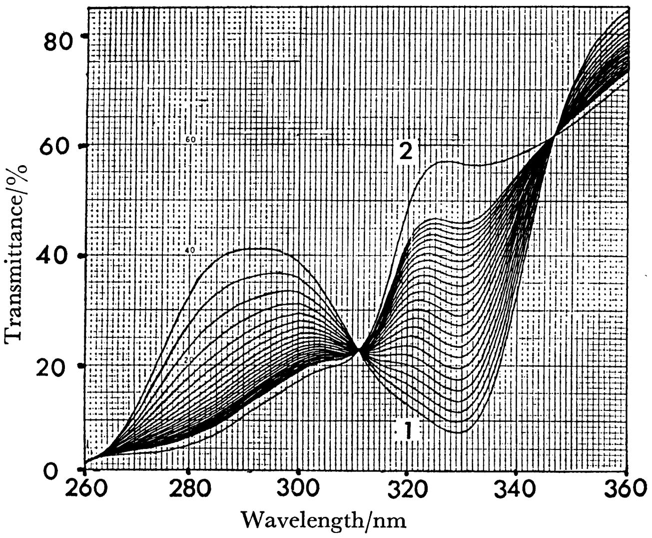

Fig. 2. The change of absorption spectrum with time during the reaction of $Pd(acac)_2$ (6.860×10^{-5} mol dm^{-3}) with diethylamine (2.039×10^{-1} mol dm^{-3}) in THF at 25.0 °C, curves 1 and 2 being spectra 2 min and *ca.* 4 h after commencement of the reaction, respectively.

Table 1. Pseudo first order rate constants for the reactions of $Pd(acac)_2$ with amines at 25 °C

Solvent	$10^5[Pd(acac)_2]$ / mol dm^{-3}	10^2[amine] / mol dm^{-3}	10^3k_{obsd} / s^{-1}
		butylamine	
CH_3OH	8.925	0.3475	1.60
		0.4545	2.05
		0.6621	2.77
		0.7848	3.33
		1.059	4.36
		1.324	5.37
		2.119	8.28
		cyclohexylamine	
	9.104	0.1753	0.742
		0.2566	0.924
		0.5006	1.54
		0.6632	1.92
		0.9340	2.66
		1.151	3.20
		1.476	3.93
		1.802	4.63
		dipropylamine	
	9.012	1.741	1.47
		2.176	1.76
		2.611	1.99
		2.901	2.22
		3.482	2.59
C_6H_6	8.431	27.53	0.4669
		59.00	1.710
		68.33	2.365
	11.10	42.93	0.9471
		91.86	4.467
		diethylamine	
CH_3OH	6.198	1.600	1.62
		2.188	2.19
		3.733	3.20
	7.273	0.8615	1.10
		1.354	1.58
		1.586	1.69
	7.622	1.805	1.75
		2.557	2.29
		2.858	2.48
		4.362	3.64
	50.12	1.285	1.34
		1.531	1.60
		3.365	3.10
C_6H_6	7.458	17.74	0.4332
		32.39	1.121
		46.08	2.110
	11.28	44.54	1.977
		55.67	3.302
		74.23	5.086
		89.08	7.471
		133.6	15.69
THF	6.860	20.39	0.636
		28.88	1.22
		34.66	1.61
		51.99	3.25
		69.32	5.44

spectrum with time during the reaction of $Pd(acac)_2$ with excess diethylamine in THF at 25 °C. Two distinct isosbestic points are observed at 311 and 347 nm, and curve 2 recorded *ca.* 4 h after the commencement of reaction coincides with the spectrum of authentic $[Pd(acac)(Et_2NH)_2](acac)$. These facts indicate that the overall reaction followed spectrophotometrically is expressed by Eq. 1 and there is no absorbing species involved in an appreciable amount except the starting and final complexes.

$$Pd(acac)_2 + 2Et_2NH \longrightarrow [Pd(acac)(Et_2NH)_2](acac) \qquad (1)$$

Plots of $\log(A_t - A_\infty)$ *vs.* time gave straight lines over four half lives. Here A_t and A_∞ denote absorbances of the reaction mixture at time t and after completion of reaction, respectively. The same reaction in methanol and benzene also obeyed the pseudo first order kinetics.

Reactions of $Pd(acac)_2$ with other bases were carried out mainly in methanol. Reactions with cyclohexylamine and dipropylamine gave the final spectra, of which the former coincided with the spectrum of authentic $[Pd(acac)(cyhxNH_2)_2](acac)$. For the reaction with butylamine, a satisfactory spectrum at the infinite time could not be obtained owing to the succeeding reactions to yield $[Pd(BuNH_2)_4](acac)_2$, and the Guggenheim method[9] was employed to analyze the kinetic data.

Table 1 shows that the pseudo first order rate constants increase with the concentration of amine. However the exact dependence varies with the nature of solvent. As is seen in Fig. 3, the rate constants obtained from the reactions of several alkylamines in methanol increase with the amine concentration in accordance with the two term rate equation(2) which is characteristic of the ligand substitution reactions of square planar complexes which proceed according to the associative (**A**) mechanism.[10]

$$k_{obsd} = k_0 + k_1[\text{amine}] \qquad (2)$$

These straight lines gave a practically common non-zero intercept, indicating the contribution of the solvent path. As is listed in Table 2, the second order rate constants exhibit a remarkable difference between the primary and secondary amines, the former reacting several times faster than the latter. The basicities of these amines are not so different; the pK_a values of the

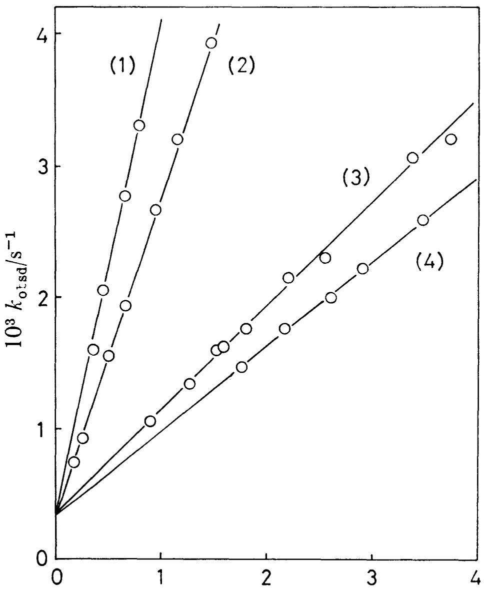

Fig. 3. Variation with the amine concentration of the pseudo first order rate constants for the reactions of $Pd(acac)_2$ with butylamine (1), cyclohexylamine (2), diethylamine (3), and dipropylamine (4) in methanol at 25 °C.

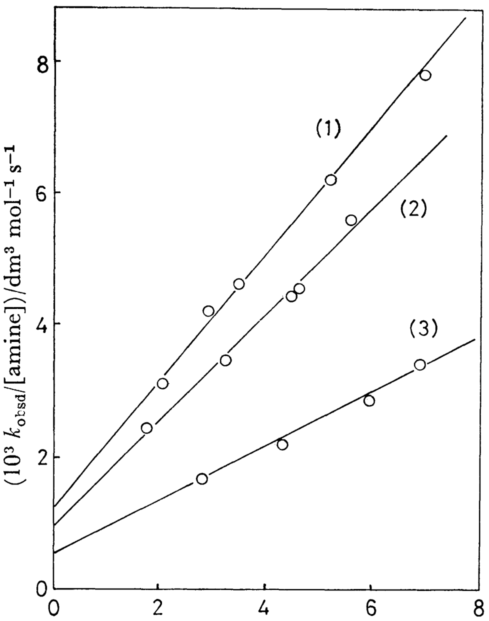

Fig. 4. Dependence on the amine concentration of the pseudo first order rate constants for the reactions of $Pd(acac)_2$ with diethylamine in THF (1) and benzene (2), and with dipropylamine in benzene (3) at 25 °C.

Table 2. Rate data for the reactions of $Pd(acac)_2$ with various amines at 25 °C

Solvent	Amine	$\frac{10^4 k_0}{s^{-1}}$	$\frac{10^2 k_1}{dm^3\,mol^{-1}\,s^{-1}}$	$\frac{10^3 k_2}{dm^6\,mol^{-2}\,s^{-1}}$
CH_3OH	butylamine	3.30±0.08	37.7 ±0.2	
	cyclohexylamine	3.32±0.07	24.3 ±0.2	
	diethylamine	3.40±0.09	8.27 ±0.09	
	dipropylamine	3.48±0.09	6.40 ±0.08	
THF	diethylamine		0.114±0.009	9.75±0.11
C_6H_6	diethylamine		0.094±0.007	8.10±0.08
	dipropylamine		0.035±0.007	4.80±0.07

conjugate acids are recorded as 10.64, 10.64, 10.93, and 11.00 at 25 °C for butylamine, cyclohexylamine, diethylamine, and dipropylamine, respectively.[11] The weaker nucleophilicity of the secondary amines than the primary amines seems to stem from their bulkiness. Steric influences of the entering as well as the leaving ligands have been established for amine substitution reactions of some platinum(II) complexes.[12]

On the other hand, the kinetic data obtained for the secondary amines in benzene and THF did not give linear plots similar to those in Fig. 3, but instead gave straight lines when $k_{\mathrm{obsd}}/[\mathrm{amine}]$ was plotted against the amine concentration (Fig. 4), thus conforming to Eq. 3.

$$k_{\mathrm{obsd}} = (k_1 + k_2[\mathrm{amine}])[\mathrm{amine}] \qquad (3)$$

In these non-coordinating solvents the solvent path is not observed. The first term in Eq. 3 may correspond to the second term in Eq. 2, representing the reagent path. It should be noted, however, that the values of k_1 for the reactions of diethylamine in benzene and THF are about 1/80 of k_1 in methanol and k_1 for the dipropylamine reaction in benzene is less than 1/180 of that in methanol (Table 2). The k_2 path showing the second order dependence of the rate on the amine concentration has not been observed for usual substitution reactions of the square planar complexes. Some kind of specific interaction between $\mathrm{Pd(acac)_2}$ and amine might assist the displacement of the acetylacetonate ligand. Table 3 lists the rate constants for the reaction of diethylamine at various temperatures and the kinetic parameters obtained from the Eyring plots.

TABLE 3. RATE CONSTANTS AT VARIOUS TEMPERATURES AND KINETIC PARAMETERS FOR THE REACTION OF $\mathrm{Pd(acac)_2}$ WITH DIETHYLAMINE

	10^2k_1 in $\mathrm{CH_3OH}$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	10^3k_1 in $\mathrm{C_6H_6}$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	10^3k_2 in $\mathrm{C_6H_6}$ $\mathrm{dm^6\ mol^{-2}\ s^{-1}}$
25 °C	8.27±0.09	0.94±0.07	8.10±0.08
30 °C	9.59±0.10	1.07±0.10	10.1±0.1
35 °C	10.3 ±0.1	1.24±0.11	11.9±0.2
40 °C	11.8 ±0.2	1.51±0.12	13.5±0.2
ΔH^{*}/KJ mol^{-1}	15±1	21±2	23±1
ΔS^{*}/J K^{-1} mol^{-1}	−20±4	−33±5	−9±5

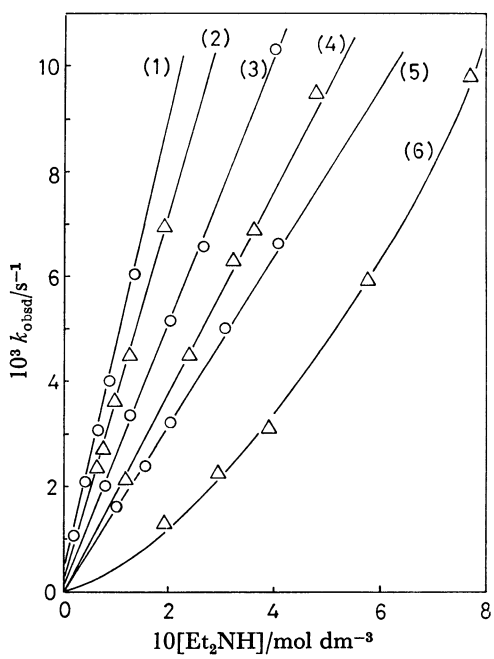

Fig. 5. Variation with the amine concentration of the pseudo first order rate constants for the reactions of $\mathrm{Pd(acac)_2}$ with diethylamine in methanol-THF mixed solvents containing 12.4 mol dm^{-3} (1), 8.24 mol dm^{-3} (2), 4.12 mol dm^{-3} (3), 2.25 mol dm^{-3} (4), 1.18 mol dm^{-3} (5), and 0.485 mol dm^{-3} (6) methanol at 25 °C.

TABLE 4. RATE DATA FOR THE REACTIONS OF $\mathrm{Pd(acac)_2}$ WITH DIETHYLAMINE IN MIXTURES OF METHANOL AND THF AT 25 °C

Mole fraction of $\mathrm{CH_3OH}$	$[\mathrm{CH_3OH}]$ / mol dm^{-3}	$10^4 k_0$ / s^{-1}	$10^2 k_1$ / dm^3 mol^{-1} s^{-1}	$10^2 k_2$ / dm^6 mol^{-2} s^{-1}
1	24.7	3.40±0.09	8.27±0.09	
0.668	12.4	1.92±0.10	4.66±0.05	
0.501	8.24	1.04±0.10	3.58±0.04	
0.263	4.12	0.45±0.11	2.56±0.04	
0.151	2.25		2.07±0.02	
0.082	1.18		1.60±0.02	
0.034	0.485		0.439±0.011	1.05±0.01
0	0		0.114±0.009	0.975±0.011

With the aim of gaining an insight into the solvent effect, the reaction of $\mathrm{Pd(acac)_2}$ with diethylamine was followed in mixtures of methanol and THF at various compositions. Figure 5 indicates that the rate equation (1) holds for the reactions in mixed solvents containing more than 4 mol dm^{-3} methanol, giving the k_0 and k_1 values as listed in Table 4. When the methanol content is as low as 0.485 mol dm^{-3}, on the other hand, the rate data deviate remarkably from linearity, but conform to the rate law (3) with $k_1 = 4.39\times10^{-3}$ dm^3 mol^{-1} s^{-1} and $k_2 = 1.05\times10^{-2}$ dm^6 mol^{-2} s^{-1}. The rate data in solutions containing 2.25 and 1.18 mol dm^{-3} methanol well lie on straight lines, but gave negative k_0 values. The quadratic term with respect to the amine concentration might contribute to the observed rates progressively with increase in the amine concentration, thus making slopes of the straight lines steeper than expected from Eq. 2. In the region where the methanol concentration is smaller than 1 mol dm^{-3}, k_1 decreases suddenly and the k_2 term contributes appreciably to the overall rate.

Kinetics of the Reaction of Acetylacetonato(acetylacetonato-C^3*)(diethylamine)palladium(II) with Diethylamine.* Although the spectral change exemplified by Fig. 2 appears to correspond to a simple reaction, the reaction of $\mathrm{Pd(acac)_2}$ with two molecules of amine such as Eq. 1 can not occur as an elementary reaction, but must consist of at least two steps, involving an intermediate which contains a unidentate acetylacetonate ligand.

$$\mathrm{Pd(acac)_2} + \mathrm{Et_2NH} \longrightarrow \mathrm{Pd(acac)_2(Et_2NH)} \qquad (4)$$

$$Pd(acac)_2(Et_2NH) + Et_2NH \longrightarrow [Pd(acac)(Et_2NH)_2](acac) \qquad (5)$$

As stated already, the reaction of $Pd(acac)_2$ with diethylamine in the preparative scale gave $Pd(acac)(acac\text{-}C^3)(Et_2NH)$ in a high yield.[2] In order to clarify whether the carbon-bonded acetylacetonato complex is involved as an intermediate in reaction (1), the rate of reaction (6) was measured in methanol at 25 °C.

$$Pd(acac)(acac\text{-}C^3)(Et_2NH) + Et_2NH \longrightarrow [Pd(acac)(Et_2NH)_2](acac) \qquad (6)$$

The pseudo first order rate constants listed in Table 5 conform to the two term rate law (2) with $k_0=(9\pm3)\times10^{-6}\ s^{-1}$ and $k_1=(9.70\pm0.08)\times10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$. Contribution of the solvent path (k_0) is negligibly small and the value of k_1 is two orders of magnitude smaller than that for the overall reaction (1). Thus the mixed-ligand complex containing a carbon-bonded acetylacetonate anion can not be an intermediate in reaction (1).

Table 5. Pseudo first order rate constants for the reaction of $Pd(acac)(acac\text{-}C^3)Et_2NH$ with diethylamine in methanol at 25 °C

10^5[complex] mol dm^{-3}	[amine] mol dm^{-3}	$10^4\ k_{obsd}$ s^{-1}
11.08	0.656	6.19
	0.765	7.50
	1.129	10.7
8.524	0.921	8.64
	1.301	12.20

Equilibrium Studies. When a solution of $[Pd(acac)(Et_2NH)_2](acac)$ in dichloromethane was kept standing for 24 h at 25 °C, an equilibrium was attained. Concentrations of three complexes involved were determined spectrophotometrically and used to calculate the equilibrium constants. The least-squares treatment of six sets of data gave the values $K_1=32.9\pm1.1\ dm^6\ mol^{-2}$ for

$$Pd(acac)_2 + 2Et_2NH \xrightleftharpoons{K_1} [Pd(acac)(Et_2NH)_2](acac) \qquad (7)$$

and $K_2=0.224\pm0.007\ dm^3\ mol^{-1}$ for

$$Pd(acac)(acac\text{-}C^3)(Et_2NH) + Et_2NH \xrightleftharpoons{K_2} [Pd(acac)(Et_2NH)_2](acac). \qquad (8)$$

Similar experiments were also performed in methanol, but the carbon-bonded complex was not involved in the equilibrium mixtures, the spectra being analyzed almost satisfactorily as mixtures of $Pd(acac)_2$ and $[Pd(acac)(Et_2NH)_2](acac)$. A more precise value of K_1 in methanol at 25 °C was obtained as $(3.93\pm0.04)\times10^6\ dm^6\ mol^{-2}$ from seven determinations started with a mixture of $Pd(acac)_2$ and diethylamine. The value is five orders of magnitude larger than that in dichloromethane, indicating an overwhelming stability of the salt-like complex in polar solvents such as methanol. In dichloromethane, on the other hand, the salt-like complex is unfavorable and converted into the carbon-bonded complex.

In order to see whether the carbon-bonded acetylacetonate can be transformed to the usual *O,O'*-chelate, *ca.* 10^{-5} mol dm^{-3} solutions of $Pd(acac)(acac\text{-}C^3)(Et_2NH)$ in dichloromethane and methanol were left standing. Spectroscopic assays at intervals over a period of several hours revealed no sign of production of $Pd(acac)_2$ but a slow decomposition was noticed. Thus the direct mutual conversion between the *O,O'*-chelated and the central-carbon-bonded states of acetylacetonate in palladium(II) complexes does not occur at all, but is reallized only *via* the outer-sphere complex.

Discussion

Kinetic studies on the bonding mode transformation of the β-diketonate ligand in metal complexes have scarcely been performed. Fish prepared a two-coordinate mercury(II) complex of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione and determined the rates at several temperatures of transformation of one of the two central-carbon-bonded ligands to the unidentate oxygen-bonding by means of the ^1H NMR spectroscopy.[13] He suggested a *C,C,O*-trihapto transition state for the intramolecular keto-enol tautomerization. Ito, *et al.* determined rates and kinetic parameters of three steps in the following reactions by ^1H NMR.[14]

$$Pt(acac)_2 \xrightarrow{+py} Pt(acac)(acac\text{-}C^3)py \underset{-py}{\overset{+py}{\rightleftharpoons}} Pt(acac\text{-}C^3)_2(py)_2 \qquad (9)$$

They also presumed a η^3-oxoallylic intermediate for the conversion of the *O,O'*-chelate to central-carbon-bonding.

In the present palladium(II) case, however, the kinetic studies unequivocally denies the intramolecular mechanism and supports the intermolecular one, one of the chelated acetylacetonate ligands leaving the coordination sphere first (Eq. 7), and then making a counterattack upon the metal atom as a carbanion (the reverse reaction of Eq. 8). Nucleophilic attack by the acetylacetonate carbanion upon the coordinated organic ligand has been occasionally demonstrated.[15,16] Although similar reactions of acetylacetonate with metal centers have not been documented explicitly thus far, the nucleophilic attack of the carbanion must be involved in preparation of the carbon-bonded acetylacetonato complexes with various metal ions.[1]

Reaction (8) is reversible and the carbon-bonded acetylacetonate can be displaced by an amine molecule. Thus formation and dissociation of the carbon-bonded acetylacetonate complex proceed *via* the outer-sphere complex, and the former can not be an intermediate in the formation reaction of the latter from $Pd(acac)_2$. The exact nature of the unidentate bonding of acetylacetonate in the intermediate complex (Eq. 4) is not clear, since the intermediate is not involved in an appreciable amount to allow the spectroscopic detection. However, the acetylacetonate in question may be bonded to palladium *via* an oxygen atom. Such an ether-like bonding was first reported for the trialkyl(acetylacetonato-*O*)silicon complexes,[17] and was more recently found in Pt(acac-*O*)$_2$(PEt$_3$)$_2$[18] and Pt(acac-*O*)$_2$(piperidine)$_2$.[19]

Pearson and Johnson[20] studied hydrolysis and other substitution reactions of Pd(acac)$_2$ in 91% water—9% methanol. A rapid equilibrium is assumed between the starting bis-chelate and an intermediate containing an oxygen-unidentate acetylacetonate ligand, which is displaced by a water molecule in the succeeding rate determining step. If this is the case for the present system, that is, if reaction (4) proceeds much faster and (5) is rate-determining, then reaction (4) should attain an equilibrium. When the equilibrium concentration of the intermediate is not negligibly small, it should be detected spectrophotometrically. On the other hand, when the equilibrium is not favorable to the intermediate, its concentration will increase with amine and the overall rate should be second order with respect to amine. In reality, the intermediate is not observed (Fig. 2) and the second order rate concerning amine is not observed for reactions in methanol. Thus reaction (4) is considered to be rate-determining, (5) proceeding faster.

The rate equation obtained in methanol (Eq. 2) and that in THF and benzene (Eq. 3) differ from each other. Although Eq. 2 involves the solvent term, Eq. 3 does not in spite of the fact that the donor number of THF (20.0) is similar to that of methanol (19.0).[21] Furthermore, k_1 which expresses the rate of the so-called reagent path increases quite remarkably when methanol is added to THF (Table 4). These results suggest some kind of interaction between Pd(acac)$_2$ and methanol to assist the attack of an amine molecule upon the palladium atom and/or the splitting of the Pd–O(acac) bond. Davis and Fackler showed from IR measurements that methanol forms hydrogen bonds with β-diketone chelates of various metal ions.[22] Recently Murthy and Shah found a slight blue shift and absorbance increase in the spectrum of tetrakis(acetylacetonato)thorium(IV) in dichloromethane on addition of methanol and other alcohols, and determined equilibrium constants for the adduct formation reactions, K for methanol being 2.0 dm^3 mol^{-1} at 30.0 °C.[23] Unfortunately the present Pd(acac)$_2$—methanol system showed no appreciable IR or electronic spectral change, but the hydrogen bond formation between them is conceivable and the scheme depicted in the upper part of Fig. 6 is proposed to the reaction in methanol. Analogously the second order term in Eq. 3 is presumed to originate from the hydrogen-bond interaction between Pd(acac)$_2$ and amine, and the lower part of Fig. 6 is proposed to the reaction in aprotic solvents.

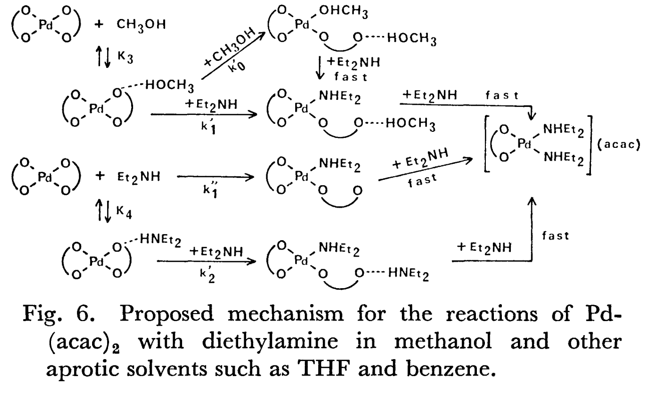

Fig. 6. Proposed mechanism for the reactions of Pd(acac)$_2$ with diethylamine in methanol and other aprotic solvents such as THF and benzene.

According to the proposed scheme the pseudo first order rate constant is calculated to be

$$k_{\text{obsd}} = \frac{k_0'K_3[\text{CH}_3\text{OH}]^2+(k_1'K_3[\text{CH}_3\text{OH}]+k_1''+k_2'K_4[\text{amine}])[\text{amine}]}{1+K_3[\text{CH}_3\text{OH}]+K_4[\text{amine}]}. \tag{10}$$

For the reaction in THF or benzene, this reduces to

$$k_{\text{obsd}} = \frac{(k_1''+k_2'K_4[\text{amine}])[\text{amine}]}{1+K_4[\text{amine}]}, \tag{11}$$

which coincides with Eq. 3 when $1 \gg K_4$[amine], resulting in

$$k_1 = k_1'' \text{ and } k_2 = k_2'K_4. \tag{12}$$

In methanol $K_3[\text{CH}_3\text{OH}] \gg 1+K_4[\text{amine}]$, that is all of the Pd(acac)$_2$ molecules are presumed to interact with methanol, and Eq. 10 reduces to Eq. 2, k_0 and k_1 being $k_0'[\text{CH}_3\text{OH}]$ and k_1', respectively.

For reactions in mixed solvents which obey the rate equation (2) rather than (3), the pseudo first order rate constant will be expressed by

$$k_{\text{obsd}} = \frac{k_0'K_3[\text{CH}_3\text{OH}]^2+(k_1'K_3[\text{CH}_3\text{OH}]+k_1'')[\text{amine}]}{1+K_3[\text{CH}_3\text{OH}]}, \tag{13}$$

giving, on comparison with Eq. 2,

$$k_0 = \frac{k_0'K_3[\text{CH}_3\text{OH}]^2}{1+K_3[\text{CH}_3\text{OH}]} \tag{14}$$

$$\frac{[\text{CH}_3\text{OH}]}{k_0} = \frac{1}{k_0'} + \frac{1}{k_0'K_3[\text{CH}_3\text{OH}]},$$

and

$$k_1 = \frac{k_1'K_3[\text{CH}_3\text{OH}]+k_1''}{1+K_3[\text{CH}_3\text{OH}]} \tag{15}$$

$$\frac{1}{k_1-k_1''} = \frac{1}{k_1'-k_1''} + \frac{1}{(k_1'-k_1'')K_3[\text{CH}_3\text{OH}]}.$$

Although the plot of $[\text{CH}_3\text{OH}]/k_0$ *vs.* $1/[\text{CH}_3\text{OH}]$ shows a straight line except one point (Fig. 7), the k_0 data are insufficient and include larger uncertainties with

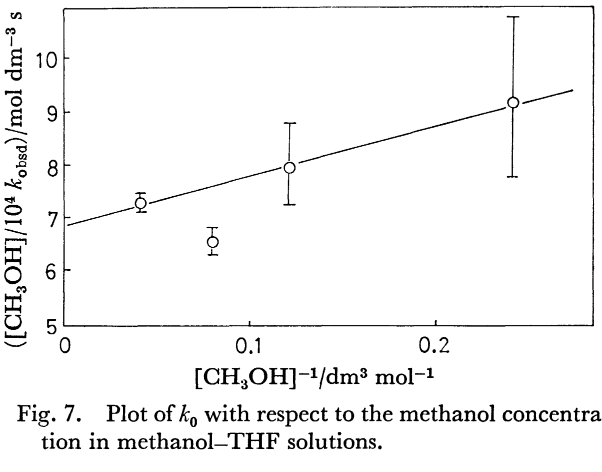

Fig. 7. Plot of k_0 with respect to the methanol concentration in methanol–THF solutions.

decreasing methanol concentration, precluding assignment of reliable values to k_0' and K_3. The trial to find an appropriate value for k_1'' to obtain a good linear plot according with Eq. 15 has also failed. Contrary to expectation based on Eq. 15, k_1 increases almost linearly with the concentration of methanol (Table 4). The rate constants k_1' and k_1'' might change intrinsically with the nature of medium. It is regrettable that various kinds of solvents can not be used for the present reaction owing to the solubility trouble.

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