November, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (11), 3257—3264 (1976) 3257

Studies on the Reacions of Bis(acetylacetonato)platinum(II) with Lewis Bases. II. Reaction with Pyridine Leading to Complexes Containing Uni- and Bis-Carbon Bonded Acetylacetonato Ligand(s).

Takashi Ito, Takashi Kiriyama, Yoshiyuki Nakamura, and Akio Yamamoto

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

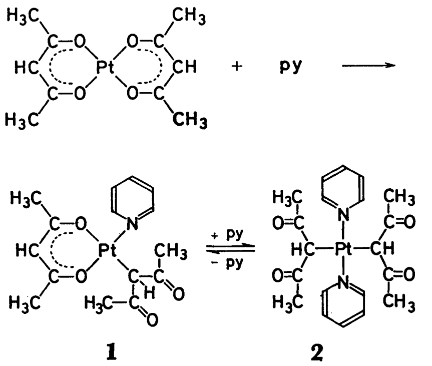
(Received June 23, 1976)

Heating a pyridine solution of [Pt(acac)$_2$] (acac=2,4-pentanedionato-*O,O′*) at 100 °C afforded central C-bonded complexes, [Pt(acac)(γ-acac)py], **1**, and [Pt(γ-acac)$_2$py$_2$], **2** (γ-acac=2,4-pentanedionato-C^3). Complexes **1** and **2** were isolated and characterized by means of elemental analysis, infrared and ^{1}H- and ^{13}C-NMR spectroscopy. Heating **1** in pyridine yielded **2**, and conversely, heating **2** in CDCl$_3$ yielded **1**. All these reactions were monitored by ^{1}H-NMR spectroscopy and were found to obey the first-order rate law. From the rate constants at various temperatures, activation parameters were calculated for each reaction. Existence of isokinetic relationship among these three reactions suggests the presence of a common reaction intermediate. Observation of the variable temperature ^{1}H-NMR spectra of [Pd(acac)(γ-acac)py] in pyridine suggests that the activated intermediate may be a species having an oxygen-bonded unidentate acac ligand ("dangling" enolate ligand).

Participation of a central(γ-) carbon atom in an acetylacetonato ligand in coordination to the metal was disclosed for the first time by Hazell *et al.* in 1959 for a dimeric β-diketonato complex of platinum(IV).[1] Soon after, Mason *et al.*[2] reported that Werner's K[Pt(acac)$_2$Cl][3,4] was in fact K[Pt(acac)(γ-acac)Cl][4] in which one of two acetylacetonato ligands is coordinated to Pt(II) *via* the central(γ-) carbon atom. Since then several kinds of γ-acac complexes of platinum(II) have been reported including Na$_2$[Pt(γ-acac)$_2$X$_2$] (X=halogen),[5] K[Pt(acac)(γ-acac)$_2$],[5] and [(acac)ClPt(γ-acac)M(II)(γ-acac)PtCl(acac)] where M(II) stands for a divalent metal ion,[6,7] as well as those of Pt(IV) such as [Pt(CH$_3$)$_3$(γ-acac)(L–L)] where L–L is 2,2′-bipyridine (bpy),[8,9] and 1,10-phenanthroline (phen).[9] However, non-ionic Pt(II) complex with a carbon-bonded acetylacetonato ligand has not been known except for poorly soluble [Pt(γ-acac)X(L–L)] where L–L is a bidentate ligand such as bpy, phen, ethylenediamine (en) and 1,2-bis(diphenylphosphino)ethane (dpe).[10] In a preceding paper, we described the isolation and characterization of new, non-ionic γ-acac complexes of the type [Pt(acac)(γ-acac)L] (L=PPh$_3$ and P(C$_6$H$_{11}$)$_3$), which are formed by the reaction of bis(acetylacetonato)platinum with an equimolar amount of the tertiary phosphine.[11] The reaction of [Pt(acac)$_2$] with an excess of pyridine, on the other hand, yielded the complex in which both acetylacetonato ligands are coordinated to platinum *via* central carbon atoms, *i.e.*, [Pt(γ-acac)$_2$(py)$_2$)], **2**, together with a mono-γ-acac complex, [Pt(acac)(γ-acac)(py)], **1**, which exist as an equilibrium mixture. There is no precedent of the observation of a direct rearrangement of the acetylacetonato ligand coordinated to platinum metal from the bidentate enol type mode of coordination (acac) to the diketo type (γ-acac), although such a rearrangement has been reported for mercury(II)[12,13] and palladium(II).[14] The present report describes isolation and characterization of γ-acac complexes **1** and **2** and some results of mechanistic study on their rearrangement reaction observed by means of the ^{1}H-NMR spectroscopy.

Results and Discussion

Reaction of Bis(acetylacetonato)platinum with Pyridine. When [Pt(acac)$_2$] was heated at 100 °C in pyridine (py), a homogeneous brown solution resulted, from which colorless prisms were produced on allowing it to stand still at room temperature. The prisms were characterized as bis(2,4-pentanedionato-C^3)bispyridineplatinum(II), [Pt(γ-acac)$_2$(py)$_2$], **2**, on the basis of microanalysis, and infrared and NMR spectral results. Although a steric configuration of **2** is uncertain, the fact that 2,2′-bipyridine does not react with [Pt(acac)$_2$] is in favor of the *trans*-configuration as is shown in the following equation.



1 **2**

From the solution part of the reaction mixture, an off-white crystalline powder of (2,4-pentanedionato-C^3)(2,4-pentanedionato-*O,O′*)pyridineplatinum(II), [Pt(acac)(γ-acac)py], **1**, was precipitated on addition of hexane. If the solution is heated again at 100 °C after removal of the prisms, instead of precipitating out **1**, a further crop of prisms of **2** was obtained. Thus, repetition of these procedures for 5 times or more makes the total yield of **2** to be almost quantitative. This fact indicates that complexes **1** and **2** exist in equilibrium in a pyridine solution in agreement with the result obtained by a ^{1}H-NMR spectral study (*vide infra*).

The complexes analogous to **1**, but having tertiary phosphines with a formula of [Pt(acac)(γ-acac)L] (L=

TABLE 1. MELTING POINTS, MICRO ANALYSES, AND INFRARED SPECTRAL DATA FOR COMPLEXES **1** AND **2**

Complex		Mp[a] (°C)	Analysis[b] (%)			IR Absorptions (cm^{-1})	
			C	H	N	γ-acac bands	acac bands
[Pt(acac)(γ-acac)py]	**1**	162—164	37.8	3.92	3.01	1700s	1565s, 1545sh
			(38.1)	(4.05)	(2.97)	1655m	1525s
[Pt(γ-acac)$_2$(py)$_2$]	**2**	174—165	43.6	4.26	5.07	1650vs	
			(43.6)	(4.39)	(5.08)	1610s	

a) Melting points (with decomposition) were measured on a hot stage with a sample in a small capillary sealed under vacuum and are uncorrected. b) Calculated values are in parentheses.

PPh$_3$ and P(C$_6$H$_{11}$)$_3$) have been obtained by the reaction of [Pt(acac)$_2$] with an equimolar amount of the corresponding tertiary phosphine.[11] It is interesting to note, however, that the reaction with an excess amount of triphenylphosphine at an elevated temperature resulted in the formation of another type of platinum(II) complex of a composition [Pt(CH$_2$COCHCOCH$_3$)(PPh$_3$)$_2$],[11] instead of yielding the bis-γ-acac complex analogous to **2**. Complex **2** is the first example of a neutral Pt(II) complex in which two acetylacetonato ligands are coordinated to the metal *via* central (γ-) carbon atoms. The reaction of bis(acetylacetonato)-palladium with pyridine is known to afford only the complex analogous to **1**, *i.e.*, [Pd(acac)(γ-acac)py].[14] The formation of the palladium complex similar to **2**, [Pd(1-ethoxy-1,3-dioxobut-2-yl)$_2$L$_2$] was reported quite recently, where L stands for a substituted or unsubstituted pyridine.[15]

Infrared and ^{1}H- and ^{13}C-NMR Spectra of the Complexes. In Table 1, characteristic infrared absorptions due to the acetylacetonato ligands in complexes **1** and **2** are listed together with melting points and analytical data. A pattern of the spectrum of complex **1** in the region of 1500—1700 cm^{-1} is very similar to those reported for [Pt(acac)(γ-acac)PPh$_3$][11] and K[PtCl(acac)(γ-acac)].[16] In addition to bands listed in Table 1, there is an extra band in the spectrum of complex **1** at 1615 cm^{-1} which is assignable to the coordinated pyridine moiety. Two bands due to the γ-acac ligand in **1** appeared at a higher wave number by 15—20 cm^{-1} than in palladium analog of **1**, [Pd(acac)(γ-acac)py].[14] Absence of a band in the region of 1500—1600 cm^{-1} in complex **2** strongly suggests that it has no O-bonded chelate acac ligand. Two bands at 1650 and 1610 cm^{-1} can be assigned to ν(C=O) of the carbon bonded γ-acac ligand by comparing them with the reported values of 1652 and 1626 cm^{-1} for Na$_2$[PtCl$_2$(γ-acac)$_2$].[16] These lines of infrared spectral evidence are in accord with the bis(γ-acac) type of structure proposed for **2**.

The ^{1}H-NMR parametrs of complexes **1** and **2** are listed in Table 2. Assignments of their signals have been made simply by comparing them with those reported for the similar complexes.[5,9,11,14] Two methyl groups in the chelated enol acac ligand in **1** appear as non-equivalent signals owing to difference in the influence of the ligands *trans* to the chelate oxygen, as is the case reported for [MX(acac)L] (M=Pt[10] and Pd[14]) and [M(acac)(γ-acac)L] (M=Pd[14] and Pt[11]). According to the assignment made by Baba *et al.* for [Pd(acac)(γ-acac)L] (L=PPh$_3$, py, and *N*-methylbenzylamine),[14] the signal at higher field (δ=1.87 ppm) is tentatively assigned to the methyl group *cis* to the pyridine ligand. The methine proton of the γ-acac ligand in complex **1** resonates at a lower field than that in [Pt(acac)(γ-acac)-

TABLE 2. THE ^{1}H-NMR DATA FOR [Pt(acac)(γ-acac)py], **1**, AND [Pt(γ-acac)$_2$(py)$_2$], **2**[a]

Complexes	Assignments		δ/ppm	Multiplicity[d]	Relative intensity[b]	J/Hz
1	acac	-CH$_3$	1.87	s	2.8(3)	
			1.96	s	2.6(3)	
		$>$CH	5.50	s	1.0(1)	
	γ-acac	-CH$_3$	2.24	ss	5.5(6)	$\lvert ^4J$(Pt-H)$\rvert$=9
		$>$CH	5.05	ss	1.0(1)	$\lvert ^2J$(Pt-H)$\rvert$=129
	py	α-H	8.70	ds[e]	2.1(2)	$\lvert ^3J$(Pt-H)$\rvert$=43
		β-H	7.35	t[e]	2.9(2)[c]	
		γ-H	7.80	t[e]	1.1(1)	
2	γ-acac	-CH$_3$	1.87	ss	6.1(6)	$\lvert ^4J$(Pt-H)$\rvert$=11
		$>$CH	4.29	ss	1.0(1)	$\lvert ^2J$(Pt-H)$\rvert$=102
	py	α-H	8.45	ds[e]	2.0(2)	$\lvert ^3J$(Pt-H)$\rvert$=39
		β-H	7.44	t[e]	2.1(2)[c]	
		γ-H	7.80	t[e]	1.1(1)	

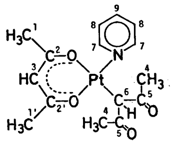
a) 100 MHz in CDCl$_3$ at room temperature, tetramethylsilane as an internal standard.
b) Required values in parentheses. c) Signals due to solvent impurities are overlapping.
d) Muliplicity abbreviations: s, singlet; ss, singlet with satellites due to ^{195}Pt; ds, doubelt with satellites due to ^{195}Pt, t, triplet. e) $\lvert ^3J$(H—H)$\rvert \approx$6 Hz.

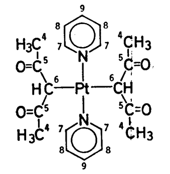
TABLE 3. ^{13}C-NMR SPECTRAL DATA OF [Pt(acac)(γ-acac)py], **1**, AND [Pt(γ-acac)$_2$(py)$_2$], **2**[a)]

Assignment[b)]			[Pt(acac)(γ-acac)py], **1**			[Pt(γ-acac)$_2$(py)$_2$], **2**		
			δ/ppm	Multiplicity[c)]	J/Hz	δ/ppm	Multiplicity[c)]	J/Hz
acac	CH$_3$	*1*	27.1	s				
	CH$_3$	*1'*	27.2	s				
	C=O	*2*	183.8	s				
	C–O	*2'*	184.8	s				
	H–C<	*3*	102.0	ss	$\lvert ^3J(\text{Pt–C})\rvert = 68$			
γ-acac	CH$_3$	*4*	30.7	s		30.5	s	
	>C=O	*5*	207.9	ss	$\lvert ^2J(\text{Pt–C})\rvert = 65$	203.1	ss	$\lvert ^2J(\text{Pt–C})\rvert = 49$
	–C–H	*6*	41.7	ss	$\lvert ^1J(\text{Pt–C})\rvert = 619$	60.3	ss	$\lvert ^1J(\text{Pt–C})\rvert = 369$
py	α-C	*7*	153.6	s		153.0	s	
	β-C	*8*	125.5	ss	$\lvert ^3J(\text{Pt–C})\rvert = 49$	126.0	ss	$\lvert ^3J(\text{Pt–C})\rvert = 49$
	γ-C	*9*	137.6	ss	$\lvert ^4J(\text{Pt–C})\rvert = 14$	138.0	s	

a) In CDCl$_3$ at room temperature, 25.1 MHz. Tetramethylsilane as an internal standard.

b) Numbering for the carbon atoms is as follows:





c) Multiplicity abbreviations: s, singlet; ss, singlet with satellite bands due to ^{195}Pt.

PPh$_3$] (4.04 ppm[11)]) by *ca.* 1 ppm whereas that in **2** resonates at the similar field. These methine protons accompanied satellite bands due to ^{195}Pt with a larger coupling constant for **1** than for **2**. Although no data are available for the ^{195}Pt–H coupling constant of the methine proton of the mutually *trans* bis(γ-acac) ligands, the $|^2J(^{195}\text{Pt–H})|$ values for **1** and **2** listed in Table 2 are similar to those reported for K[Pt(acac)(γ-acac)Cl] (120 Hz) and K[Pt(acac)(γ-acac)$_2$] (123 Hz).[5)] Assignments of the signals due to the pyridine ligand(s) were achieved by examination of their relative intensities and multiplicities. A doublet assignable to the α-proton in the coordinated pyridine accompanied satellite bands due to a coupling with ^{195}Pt.

The structures of complexes **1** and **2** are further supported by their ^{13}C-NMR spectra which are summarized in Table 3. The spectrum of complex **1** is similar to that of the analogous complex [Pt(acac)(γ-acac)PPh$_3$].[11)] Absence of the phosphorus nucleus in **1** made the spectrum more simplified than the PPh$_3$ analog. Assignment of each signal was further confirmed by recording a half decoupled spectrum,[17)] in which the signals assigned to C^3, C^6, C^7, C^8, and C^9 split into doublets while those to C^2, $C^{2'}$, and C^5 remained as singlets. (As for the numbering of the carbon atoms, refer to the foot note of Table 3). A singlet signal due to C^4 split into a quartet on half decoupling and those of C^1 and $C^{1'}$ changed to a complex pattern which is consisted of basically 8 lines. The $|^1J(^{195}\text{Pt–}^{13}\text{C})|$ value of 619 Hz for the methine carbon of the γ-acac ligand in complex **1** is similar to the reported values for *cis*-[Pt(CH$_3$)$_2$L$_2$] (594 Hz for L=PMe$_2$Ph,[18)] 689 Hz for L=AsMe$_3$,[19)] and 685 Hz for L=AsMe$_2$Ph.[18)] On the other hand, an exceptionally small $|^1J(^{195}\text{Pt–}^{13}\text{C})|$ value (369 Hz) was observed for complex **2**. Such a small ^{195}Pt–^{13}C coupling constant has been reported only for the methyl carbon attached to platinum atom at a *trans* position with respect to the carbene ligand, *i.e.*, *trans*-[Pt(CH$_3$)(cb)(AsMe$_3$)$_2$][PF$_6$], where cb stands for carbene ligands (385 Hz for cb=:CMe(NMe$_2$), 381 Hz for cb=:CMe(NHMe), 380 Hz for cb=:CMe(NH$_2$), and 360 Hz for cb=:CMe(OMe)).[19,20)] This decrease in $|^1J(\text{Pt–C})|$ value when going from **1** to **2** parallels a decrease in $|^2J(\text{Pt–H})|$ value suggesting a stronger Pt–C bond in complex **1** than in **2**. Interestingly, the slope of the line connecting two points plotted for $|^1J(\text{Pt–C})|$ *vs* $|^2J(\text{Pt–H})|$ coincided fairly well with those reported for serieses of platinum–methyl complexes.[20,21)] The keto-carbon (C^5) in the γ-acac ligand in **1** and **2** showed ^{195}Pt-satellite bands with $|^2J(\text{Pt–C}^5)| = 65$ and 49 Hz, respectively. Although there are no available data on the ^{13}C-NMR spectral parameters for this type of ligand, these values are within the range of values reported for $|^2J(\text{Pt–C})|$, *e.g.*, 50 and 86 Hz have been reported for $|^2J(\text{Pt–As–C})|$ and $|^2J(\text{Pt–C–C})|$, respectively, in the carbene complex, *trans*-[PtMe{C(OMe)Me}(AsMe$_3$)$_2$][PF$_6$].[20,21)] Furthermore, ^{195}Pt-satellite bands are observed for the methine carbon (C^3) of acac ligand with $|^3J(\text{Pt–C}^3)| \doteq 68$ Hz, which is larger than $|^2J(\text{Pt–C}^5)|$. This effect may reflect the conjugate character of the chelate acac ligand. Intensities of unequivalent C^2 and $C^{2'}$ signals were reduced considerably as compared with that of the C^3 signal due to the absence of NOE effect (C^3 being tertiary carbon), hence a discernment of its satellite bands from the noise signals might have become impossible. Among three signals due to the pyridine ligand, the signal with the smallest intensity at *ca.* 138 ppm was assigned to the

γ-carbon. Assignments of the other two signals were made by comparing their chemical shifts with those of free pyridine (149.6, 123.5 and 135.6 ppm for α, β, and γ-carbons, respectively in $CDCl_3$).[22] It should be noticed that the α-carbon signal does not accompany satellite bands due to ^{195}Pt in spite of the presence of the distinct satellite bands for β- (in **1** and **2**) and γ- (in **1**) carbon atoms. This fact may be correlated to the reported data on the phenylplatinum complex, *cis*-$[PtPh_2(PEt_3)_2]$, where the ^{195}Pt–C coupling constant due to the phenyl *ortho* carbon is less than that for *meta* carbon (36 and 64 Hz, respectively).[21] A poor resolution of the spectrum of **2** prevented the accurate measurement of the coupling constant for the γ-carbon satellite bands.

Kinetic Study on the Formation of 1 and 2. Kinetic studies on the formation of **1** and **2** and their interconversions were achieved by following the ^1H-NMR spectral change in either pyridine or chloroform at various temperatures.

The ^1H-NMR spectrum of $[Pt(acac)_2]$ in pyridine at 60 °C consists of a single methyl resonance at 1.79 ppm and a methine resonance at 5.48 ppm. (Fig. 1A). On keeping the sample at this temperature, several new signals which are assignable to the protons of γ-acac ligand(s) in **1** and **2** appeared at the expense of the initial two singlets and they grew gradually with time. Figure 1B illustrates the spectrum of the system taken after 9 h at 60 °C. Assignments of the signals were confirmed by comparing them with the spectra of the isolated complexes **1** and **2**. The rate of conversion of $[Pt(acac)_2]$ into **1** (reaction (i) in Eq. 2) obeyed the first-order rate law with respect to $[Pt(acac)_2]$. The first-order rate constants (k_1) thus obtained for reaction (i) at various temperatures are listed in Table 4. Similarly were obtained the first-order rate relationship for reactions (ii) and (iii) in Eq. 2. For reaction (ii) the

$$[\mathrm{Pt(acac)_2}] + \mathrm{py} \xrightarrow[\text{(i)}]{k_1}$$

$$\{[\mathrm{Pt(acac)(\gamma\text{-}acac)py}] \underset{-\mathrm{py},\ k_3\mathrm{(iii)}\ \text{in}\ \mathrm{CDCl_3}}{\overset{+\mathrm{py},\ k_2\mathrm{(ii)}}{\rightleftarrows}} [\mathrm{Pt(\gamma\text{-}acac)_2py_2}]\} \quad (2)$$

isolated complex **1** was dissolved in pyridine and the rate of growth of the methyl signal in the γ-acac ligand of **2** in pyridine was monitored (Fig. 2) and the first-order rate constants, k_2, thus obtained are listed in Table 4. The reverse reaction (iii) was followed by observing the spectral change of **2** in $CDCl_3$, where signals due to **1** appeared and grew gradually with time as is

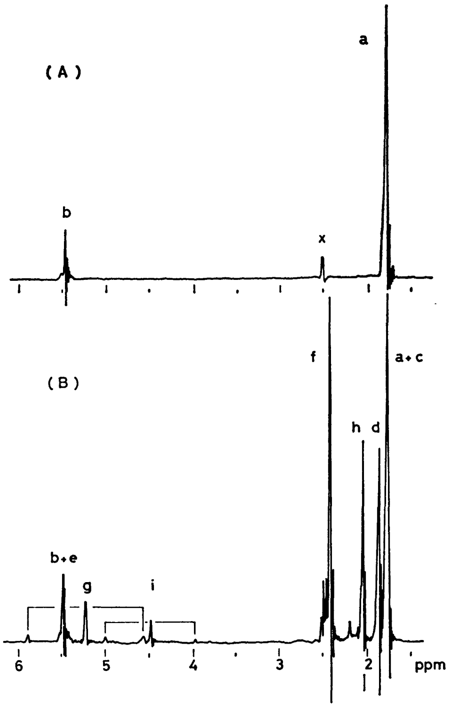
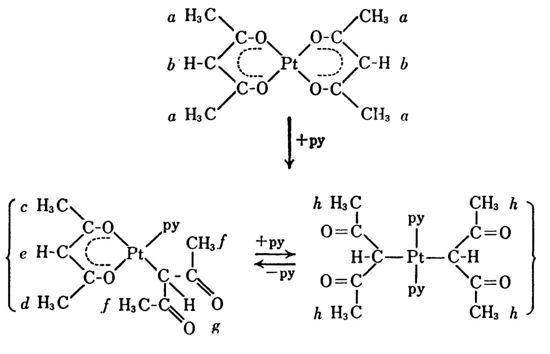


Fig. 1. Change of the ^1H-NMR spectrum (methyl and methine proton region) of $[Pt(acac)_2]$ in pyridine at 60 °C. (A) Initial spectrum. (B) After 9 h.



The signal x is assignable to γ-picoline present in the solvent as an impurity.

Table 4. First-order rate constants for the reactions (i), (ii), and (iii) (Eq. 2)

Temp. (°C)	40	50	60	70	80	90	100
$k_1 \times 10^5/s^{-1}$	—	—	4.55	13.2	28.7	54.4	118
$k_2 \times 10^5/s^{-1}$	—	1.36	2.94	6.23	12.1	—	—
$k_3 \times 10^5/s^{-1}$	0.410	—	5.10	17.1	53.7	—	—

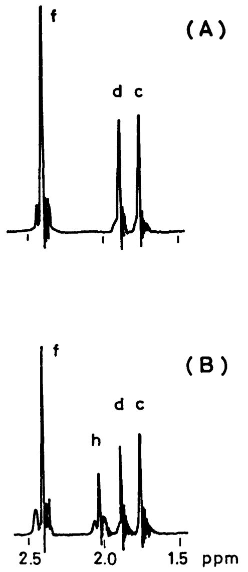


Fig. 2. Change of the ^1H-NMR spectrum (methyl proton region) of [Pt(acac)(γ-acac)py] in pyridine-d_5 at 50 °C. (A) Initial spectrum. (B) After 4 h. Proton notations are as shown in Fig. 1.

TABLE 5. ACTIVATION PARAMETERS FOR THE REACTIONS (i)—(iii) (Eq. 2) AND (iv) (Eq. 3)

Reaction	E_a kcal mol^{-1}	log A	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal K^{-1} mol^{-1}	$\Delta G^{\neq}$ (60 °C) kcal mol^{-1}
(i)	20.9±0.1	9.34±0.07	19.3±0.1	−20.7±0.2	26.2±0.2
(ii)	16.3±0.0	6.17±0.01	15.6±0.0	−32.7±0.1	26.5±0.1
(iii)	26.6±0.0	13.2±0.0	26.0±0.0	−0.36±0.10	26.1±0.1
(iv)	6.16±0.07	5.67±0.05	5.82±0.06	−33.7±0.2	16.2±0.1[a)]

a) $\Delta G^{\neq}$ at 35° C.

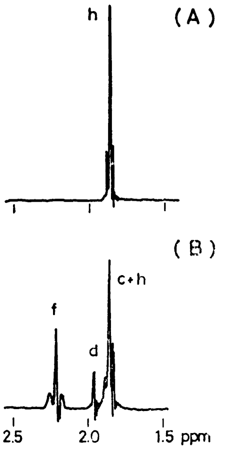
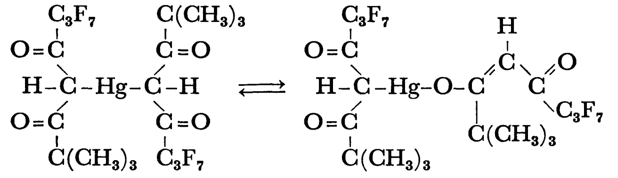


Fig. 3. Change of the ^{1}H-NMR spectrum (methyl region) of $[Pt(\gamma\text{-acac})_2py_2]$ in $CDCl_3$ at 60 °C. (A) Initial spectrum. (B) After 4.5 h. Proton notations are as shown in Fig. 1.

illustrated in Fig. 3. Deuteriochloroform was used as a reaction solvent in reaction (iii) because of a poor solubility of **2** in pyridine. The first-order rate law was again observed and the rate constants, k_3, obtained at various temperatures, are also included in Table 4. Arrhenius activation energies, E_a, and frequency factors, A, for reactions (i), (ii), and (iii) were obtained from the slopes and intercepts, respectively, of the least-square straight lines of log k *vs.* $1/T$ plots. Activation enthalpies, $\Delta H^{\neq}$, and activation entropies, $\Delta S^{\neq}$, were obtained similarly from the least-square treatment for the Eyring plots of log k/T *vs.* $1/T$. The free energy of activation, $\Delta G^{\neq}$, was calculated from the equation $\Delta G^{\neq}=\Delta H^{\neq}-T\Delta S^{\neq}$. The activation parameters are liested in Table 5.

In spite of numerous studies concerning the configurational rearrangement of octahedral enolate acetylacetonato complexes of transition and non-transition metals,23—27) scarcely has been reported the mechanistic study of the ligand exchange in the square planar acetylacetonato complex.28) This may be ascribed to the slow rate of exchange in the latter compared to the six-coordinate complex, which renders the study of dynamic behavior of these complexes by NMR measurement inapplicable. Furthermore, little has been studied on the rearrangement of acetylacetonato complex between a chelated enol form and a central carbon bonded diketo form. Fish has made an NMR study on the dynamic behavior of bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-dioxooctan-5-yl)mercury in acetone-d_6, in which the following exchange has been observed.13) The Arrhenius activation energy, E_a, and the free energy of activation, $\Delta G^{\neq}$, for this process were estimated as 9.90 and 10.35 (at 25 °C) kcal/mol*, respectively, which are much lower than the values of, respectively, 16—27 and *ca.* 26 kcal/mol for the present system, indicating a less labile character of the acac ligand in the present platinum complexes in the keto-enol exchange as compared to the mercury complex in agreement with the prediction by Fish.13)



Observation that the reactions (i), (ii), and (iii) obey the first-order rate law suggests that these reactions proceed *via* unimolecular processes with respect to the complexes involved. Furthermore, observation of constant $\Delta G^{\neq}$ values for the three reactions, despite the considerable variance of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, suggests the presence of an isokinetic relationship. Figure 4 demonstrates the presence of the compensation effect between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values in the three reactions. In a strict sense, comparison of the reactions (i) and (ii) with reaction (iii) may not be quite adequate because of the difference in the solvent employed. (Employment of $CDCl_3$ in reactions (i) and (ii) was not feasible because of occurence of unexpected, not fully studied reaction

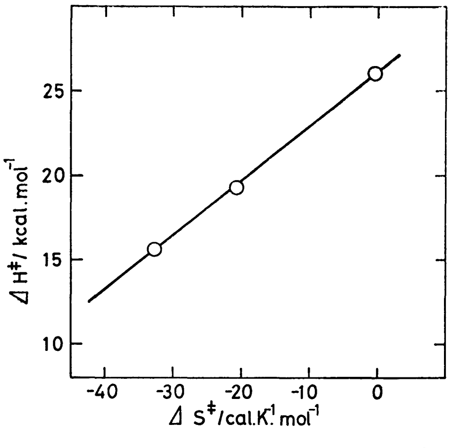


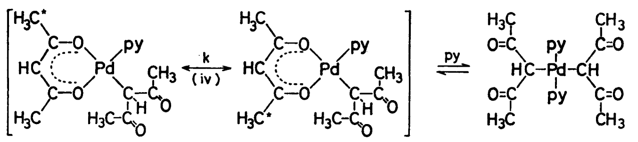
Fig. 4. Isokinetic relationship for the reactions, $[Pt(acac)_2] \xrightarrow{py} [Pt(acac)(\gamma\text{-acac})py] \underset{-py}{\overset{py}{\rightleftarrows}} [Pt(\gamma\text{-acac})_2(py)_2]$.

---

* Throughout this paper 1 cal=4.184 J.

between $CDCl_3$ and pyridine in the presence of the platinum complex.) However, the results suggest that, in spite of the difference in solvents, the three reactions proceed through a similar activated species in the rearrangement reactions from the acac form to the γ-acac form and *vice versa*. The isokinetic temperature, the temperature at which the rates of three processes become equal, was estimated as 323 K (50 °C).

In contrast to the platinum complex, the reaction of bis(acetylacetonato)palladium with pyridine has been reported to give only [Pd(acac)(γ-acac)py] even under rigorous conditions.[14] No bis(γ-acac) complex of palladium, analogous to **2**, has been isolated. The variable temperature ^{1}H-NMR measument of [Pd(acac)(γ-acac)py], **3**, in pyridine, however, revealed the presence of equilibria as follows:



A **3** B **4** (3)

Two singlets at 2.08 and 1.94 ppm at −20 °C due to the two methyl groups of the chelated acetylacetonato ligand in **3** broaden on raising the temperature and coalesce at 46 °C. Above the temperature, the coalesced singlet signal sharpens with temperature increase. This spectra change may be interpreted by assuming the acceleration of the exchange rate between species A and B on raising the temperature (Eq. 3). In Fig. 5, the relevant spectra in the temperature range of 20—46 °C are reproduced, together with the one at −20 °C. The rate constants k, for the exchange were calculated from the separation of two singlets as are recorded in Figure 5. An Arrhenius plot of these k values leads to activation parameters which are included in Table 5. A very small peak is observed at 1.99 ppm at −20 °C and it grows gradually on raising the temperature (Figure 5). This may be due to the methyl protons of bis(γ-acac) type complex **4**, which is in equilibrium with **3** (Eq. 3). All attempts to isolate **4** from the equilibrium mixture were unsuccessful.

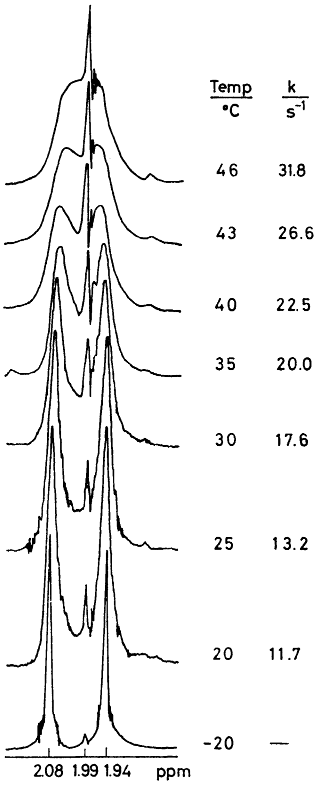
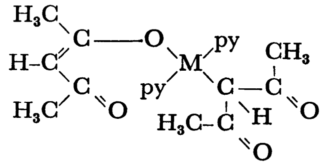


Fig. 5. Temperature dependence of the ^{1}H-NMR spectra (methyl proton region) of [Pd(acac)(γ-acac)py] in pyridine-d_5.

Saito and Takahashi have reported the Arrhenius activation energy E_a of 23 kcal/mol for the palladium–oxygen bond rupture in the exchange reaction of $[Pd(acac)_2]$ and ^{14}C-labelled acetylacetone in anisole.[28] Much smaller value (6.2 kcal/mol) obtained in the present study implies that the presence of a large excess of pyridine may facilitate the palladium–oxygen bond rupture. The presence of large negative $\Delta S^{\neq}$ values for the forward (bidentate enol→unidentate diketo) transformations and a very small $\Delta S^{\neq}$ value for the reverse process with regards to platinum complexes also may be taken as an indication of the solvent participation in the forward processes. The mechanism of the interchange may involve the solvent assisted partial M–O bond rupture as shown below, rotation of the unidentate acac around the M–O bond and recoordination *via* the carbonyl group to the metal.

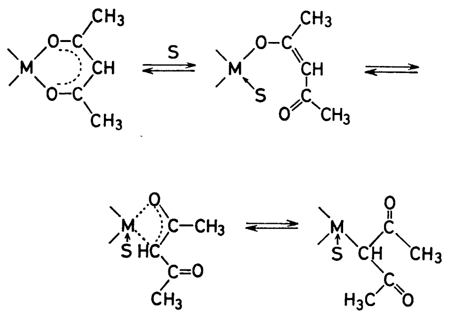


M=Pd, Pt

The similar value of E_a, *ca.* 10 kcal/mol, has been reported for the exchange of a bidentate enol acac ligand in $[NiEt(acac)PPh_3]$[29] and in the various six-coordinate acac complexes.[23,24]

In a separate reaction of $[Pt(acac)_2]$ with triethylphosphine we have isolated another type of a complex, bis(2,4-pentanedionato-*O*)bis(triethylphosphine)platinum(II) containing two unidentate acac ligands, which are singly bonded to platinum through enol oxygen atoms.[30]

In view of these results it is tempting to speculate on the rearrangement mechanisms of the acac ligand. In the forward reaction starting from the bidentate enol type complex to the γ-acac type complex three reaction pathways are conceivable. A bimolecular mechanism involving the direct transfer of the chelate acac ligand to another platinum complex is unlikely on the basis of the observed first-order rate law. The second mechanism where a unimolecular "flipping" of the bidentate enol ligand to the γ-acac ligand takes place seems less likely than the third mechanism which involves the partial dissociation of the bidentate enol ligand to a singly bonded form with participation of the solvent. The further process might involve an oxoallyl intermediate through which a new M–C bond is formed as shown below in the following scheme:



(S=solvent molecule)

The reverse process starting from the γ-diketo form leading to the enol chelate could be accounted for by assuming common intermediates presented above.

Although the evidence supporting this mechanism is circumstantial at best, it is compatible with various features of the rearrangement reaction.

Formation of a γ-acac type complex also may have implications related to the polymerization activities of various transition metal acetylacetonates for some vinyl monomers.[31,32] A typical initiator $[Mn(acac)_3]$ can be reduced to $[Mn(acac)_2]$ in the presence of a vinyl monomer which is polymerized by a radical $CH_3CO\dot{C}HCOCH_3$[31–33] liberated by homolytic splitting of Mn–C bond from a possible intermediate complex such as $[Mn(acac)_2(\gamma\text{-acac})\cdot S]$. In fact, the reduction of $[Mn(acac)_3]$ in the presence of 1,10-phenanthroline gave a phen-complex $[Mn(acac)_2(phen)]$.[33,34] Another implication of the partial dissociation of the enol chelate concerning the alkylation mechanism of transition metal acetylacetonates has been discussed in the previous paper.[11]

Experimental

Procedures, materials, and instruments used are as reported in a preceding paper.[11] Guaranteed grade pyridine was used for the reaction without further purification.

Reaction of Bis(acetylacetonato)platinum(II) with Pyridine. The pale yellow suspension of $[Pt(acac)_2]$ (0.60 g, 1.53 mmol) in pyridine (3.4 cm^3) was heated at 100—110 °C under nitrogen for 1 h resulting in a brown solution. After cooling, 20 cm^3 of hexane was added to the solution to yield a creamy white precipitate, which was filtered off, washed with hexane and dried *in vacuo*. The crude product (0.54 g) thus obtained is a mixture of $[Pt(acac)(\gamma\text{-acac})py]$, **1**, and $[Pt(\gamma\text{-acac})_2(py)_2]$, **2**, which can be separated from each other by extraction with diethyl ether ($20\ cm^3 \times 5$). The extract was concentrated to *ca.* 10 cm^3 *in vacuo*. To the concentrated solution was added hexane (20 cm^3) to give a creamy white precipitate which was filtered off, washed with hexane and dried *in vacuo*. The off-white powder thus obtained (0.34 g, 40%) was identified as $[Pt(acac)(\gamma\text{-acac})py]$, **1**, on the basis of infrared and NMR spectroscopy (see text). The product thus obtained is analytically pure, but can be recrystallized from toluene.

The white residue of extraction was found to be analytically pure $[Pt(\gamma\text{-acac})_2(py)_2]$, **2** (0.12 g, 17%). The results of micro analysis for complexes **1** and **2** are listed in Table 1.

In order to obtain **2** in a much higher yield, the following procedure is recommendable. The yellow solution of $[Pt(acac)_2]$ (0.90 g, 2.29 mmol) in pyridine (10 cm^3) was heated at 100—110 °C under nitrogen for 6 h. The system was cooled down to room temperature and kept at the temperature overnight. The colorless prisms of **2** thus yielded were isolated by decantation, washed with diethyl ether and dried *in vacuo*. (0.16 g). The supernatant was again heated at 110 °C for 3 h. On working up as above, 0.20 g of the prisms of **2** were obtained. Repetition of this procedure 5 times gave the total amount of 0.91 g (72%) of **2** obtained as colorless prisms; the procedure may be continued further until the quantitative yield of **2** is attained.

Kinetic Measurements. The kinetic measurements of the rearrangement of acetylacetonato ligand were made using a JEOL PS-100 NMR spectrometer equipped with a JES-VT-3 variable-temperature controller. The temperature of the probe was calibrated (±0.5 °C) by measuring the reading of the thermometer inserted directly into a probe. The sample solution made up with the concentration of 0.18—0.27 M was used for each run.

The extent of conversion (x) of the reactions (i), (ii), and (iii) (Eq. 2 in the text) was calculated by the equations, $x_{\rm I}=\{2[f]+[h]\}/\{[a+c]+[d]+[f]+[h]\}$, $x_{\rm II}=[h]/\{[c]+[d]+[f]+[h]\}$, and $x_{\rm III}=2[f]/\{[c]+[d]+[f]+[h]\}$, respectively, where an alphabet in a square blacket means the relative intensity of the corresponding signal shown in Figs. 1—3. First-order rate constants were obtained from the slope of the linear plots of $\ln 1/(1-x)$ *vs.* t.

The rates of the interchange of the enol acetylacetonato ligand in $[Pd(acac)(\gamma\text{-acac})py]$ in pyridine-d_5 were calculated from the differences in the chemical shifts of two methyl singlets below the coalescence temperature using Gutowsky and Holm's equation.[35] The singlet signal above the coalescence temperature could not be used for the purpose of the kinetic analyses because of the overlapping of the signal in question with that ascribable to the methyl proton of $[Pd(\gamma\text{-acac})_2(py)_2]$ (see text).

We thank the Kawakami Foundation for support.

References

1) A. C. Hazell, A. G. Swallow, and M. R. Truter, *Chem. Ind.* (*London*), **1959**, 564.

2) B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature* (*London*), **195**, 1278 (1962); R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc., A*, **1969**, 485.

3) A. Werner, *Ber.*, **34**, 2584 (1901).

4) Abbreviations acac and γ-acac are used throughout this paper to indicate the chelate O-bonded enol type and unidentate central (γ-) carbon bonded diketo type 2,4-pentanedionato (acetylacetonato) ligands, respectively.

5) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, **1965**, 6740.

6) J. Lewis and C. Oldham, *J. Chem. Soc., A*, **1966**, 1456.

7) Y. Nakamura and K. Nakamoto, *Inorg. Chem.*, **14**, 63 (1975).

8) A. G. Swallow and M. R. Truter, *Proc. R. Soc. London, Ser. A*, **266**, 527 (1962).

9) J. R. Hall and G. A. Swile, *J. Organomet. Chem.*, **47**, 195 (1973).

10) G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., A*, **1970**, 1732.

11) T. Ito, T. Kiriyama, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3250 (1976).

12) K. Flatau and H. Musso, *Angew. Chem.*, **82**, 390 (1970).

13) R. H. Fish, *J. Am. Chem. Soc.*, **96**, 6664 (1974).

14) S. Baba, T. Ogura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **47**, 665 (1974).

15) S. Okeya, S. Kawaguchi, N. Yasuoka, Y. Kai, and N.

Kasai, Abstr. No. 85, 23rd Symposium on Organometallic Chemistry, Japan, Tokyo, October 1975.

16) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **7**, 330 (1968).

17) White-noise decoupled and half decoupled ^{13}C-NMR spectra of complex **2** were recorded on JEOL FX-60 by Mr. K. Kosaka of JEOL Ltd., to whom we are indebted.

18) A. J. Cheney, B. E. Mann, and B. L. Shaw, *Chem. Commun.*, **1971**, 431.

19) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, **1971**, 1627.

20) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **95**, 8574 (1973).

21) B. E. Mann, *Adv. Organomet. Chem.*, **12**, 135 (1974).

22) R. J. Cushley, D. Naugler, and C. Ortiz, *Can. J. Chem.*, **53**, 3419 (1975).

23) N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972), and references cited therein.

24) (a) N. Serpone and R. Ishayek, *Inorg. Chem.*, **13**, 52 (1974); (b) N. Serpone and K. A. Hersh, *ibid.*, **13**, 2901 (1974).

25) D. R. Herrington and L. J. Boucher, *Inorg. Chem.*, **12**, 2378 (1973).

26) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **13**, 1309 (1974).

27) (a) K. Saito and M. Murakami, *Bull. Chem. Soc. Jpn.*, **45**, 2472 (1972); (b) T. Inoue and K. Saito, *ibid.*, **46**, 2417 (1973); (c) K. Matsuzawa and K. Saito, *ibid.*, **46**, 2777 (1973); (d) A. Nagasawa and K. Saito, *ibid.*, **47**, 131 (1974); (e) C. Chatterjee, K. Matsuzawa, H. Kido, and K. Saito, *ibid.*, **47**, 2809 (1974); (f) T. Inoue, J. Fujita, and K. Saito, *ibid.*, **48**, 1228 (1975); (g) M. Nishizawa, H. Kido, I. Kinoshita, Y. Soma, and K. Saito, *ibid.*, **49**, 819 (1976).

28) K. Saito and M. Takahashi, *Bull. Chem. Soc. Jpn.*, **42**, 3462 (1969).

29) T. Yamamoto, T. Saruyama, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 589 (1976).

30) T. Ito, T. Kiriyama, and A. Yamamoto, *Chem. Lett.*, **1976**, 835.

31) C. H. Bamford and D. J. Lind, *Proc. R. Soc. London, Ser. A*, **302**, 145 (1968).

32) K. Kaeriyama, *Bull. Chem. Soc. Jpn.*, **43**, 1511 (1970).

33) K. Kaeriyama, *Makromol. Chem.*, **150**, 189 (1971).

34) K. Kaeriyama, *Bull. Chem. Soc. Jpn.*, **47**, 753 (1974).

35) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).