Palladium(II) Complexes Derived from the Reactions of Bis-(3-hydroxy-2-methyl-4-pyronato)palladium(II) with Several Nitrogen Bases

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(Received November 8, 1978)

The preparation and properties of the palladium(II) amine complexes containing 3-hydroxy-2-methyl-4-pyronate ions as the counter anions, $[Pd(N)_4]L_2$ and $[Pd(NN)_2]L_2 \cdot nH_2O$, are reported, where N=propylamine or benzylamine, NN=ethylenediamine, trimethylenediamine or *N,N*-dimethylethylenediamine, HL=3-hydroxy-2-methyl-4-pyrone, and n=2—4. The unidentate-amine complex, $[Pd(N)_4]L_2$, reacts with NaI to afford $[PdI_2(N)_2]$, whereas the bidentate-amine complex, $[Pd(NN)_2]L_2 \cdot nH_2O$, reacts with NaI to give $[Pd(NN)_2]I_2$. The mixed-ligand complexes, [PdL(bpy)]X and [PdL(phen)]X (where bpy=2,2′-bipyridine, phen=1,10-phenanthroline, X=ClO_4 or $B(C_6H_5)_4$), are also reported. On the basis of the PMR spectra, the IR spectra, and the electric conductivities, the structures of the isolated complexes are discussed.

3-Hydroxy-2-methyl-4-pyrone (HL) has some resemblance to the β-diketones, all being monobasic acids and usually functioning as O,O′-chelating agents.[1,2] The bis-chelates of these ligands with bivalent metal ions, such as Co(II), Ni(II), and Zn(II), react with nitrogen bases to form five- or six-coordinate adducts.[3,4] On the other hand, the corresponding Pd(II) complexes, $[Pd(\beta\text{-dik})_2]$, react with an excess of amine to afford $[Pd(\beta\text{-dik})(amine)_2](\beta\text{-dik})$ or $[Pd(amine)_4](\beta\text{-dik})_2$, depending upon whether the amine is secondary or primary respectively.[5] As was reported in a preliminary communication,[6] the Pd(II) complex of 3-hydroxy-2-methyl-4-pyrone, PdL_2, also reacts with ethylenediamine to result in $[Pd(en)_2]L_2 \cdot 2H_2O$. As an extension of this study, the present paper will report on the syntheses and properties of several Pd(II) amine complexes containing the 3-hydroxy-2-methyl-4-pyronate anion as a counter ion. The complexes obtained by the reactions of the above Pd(II) amine complexes with sodium iodide or lithium bromide will also be described.

Experimental

*Preparation of Complexes. Bis(3-hydroxy-2-methyl-4-pyronato)palladium(II), $[PdL_2]$ (**1**).* Palladium(II) chloride (10 mmol) was dissolved in a hot aqueous solution (100 ml) of NaCl (15 g), after which the mixture was cooled to 0—5 °C in an ice-bath. Into this solution we then vigorously stirred, a cold aqueous solution (0—5 °C, 50 ml) containing HL (20 mmol) and NaOH (20 mmol). A brown precipitate was formed immediately. After the solution had been stirred for 1 h at room temperature, a crude precipitate was filtered; this was then dissolved in chloroform (400 ml) at 40—50 °C. After the filtration of the insoluble materials, the solvent was evaporated at 35 °C. The brown residue was washed with ethanol and ether and then dried *in vacuo*. Yield: 86 %.

*Tetrakis(propylamine)palladium(II) 3-Hydroxy-2-methyl-4-pyronate, $[Pd(pa)_4]L_2$ (**2a**):* Complex **1** (1.5 mmol) was dissolved in 10 ml of benzene containing propylamine (8 mmol) at room temperature. After the removal of the insoluble materials by filtration, the solvent was evaporated at *ca.* 25 °C. A white residue was collected on a glass filter, washed with cold acetone, and dried *in vacuo*. Yield: 40 %. By using benzylamine instead of propylamine, a white precipitate of $[Pd(ba)_4]L_2$ (**2b**) was also obtained in a 50 % yield.

*Bis(ethylenediamine)palladium(II) 3-Hydroxy-2-methyl-4-pyronate Dihydrate, $[Pd(en)_2]L_2 \cdot 2H_2O$ (**3a**):* To a stirred suspension of Compound **1** (1.5 mmol) in chloroform (10 ml) we added a chloroform solution (10 ml) of ethylenediamine (10 mmol), after which the mixture was stirred for 30 min. A pale yellow precipitate was filtered and washed with cold ethanol and ether. The precipiate was then dissolved in warm ethanol (15 ml). After the removal of the insoluble materials by filtration, ether (100 ml) was added to the pale yellow filtrate. The white precipitate thus obtained was filtered, washed with cold ethanol and ether, and then dried *in vacuo*. Yield: 64 %.

*Bis(trimethylenediamine)palladium(II) 3-Hydroxy-2-methyl-4-pyronate-Water(1/2.5), $[Pd(tn)_2]L_2 \cdot 2.5H_2O$ (**3b**):* To a stirred suspension of Compound **1** (1.5 mmol) in benzene (6 ml) we added a benzene solution (20 ml) of trimethylenediamine (40 mmol), after which the mixture was stirred for *ca.* 2 h. The crude pale yellow precipitate thus obtained was filtered and washed with ether. The precipitate was then dissolved in ethanol (15 ml). After the removal of the insoluble materials by filtration, ether (150 ml) was added to the pale yellow filtrate to obtain a white precipitate, which was then filtered washed with ether, and dried *in vacuo*. Yield: 67 %.

*Bis(N,N-dimethylethylenediamine)palladium(II) 3-Hydroxy-2-methyl-4-pyronate Tetrahydrate, $[Pd(N,N\text{-}Me_2en)_2]L_2 \cdot 4H_2O$ (**3c**):* To a stirred suspension of Compound **1** (1.5 mmol) in benzene (6 ml) we added a benzene–ethanol (5:2 by volume) solution (14 ml) containing *N,N*-dimethylethylenediamine (10 mmol), after which the mixture was stirred for *ca.* 1 h. After the removal of the insoluble materials by filtration, the solvent was evaporated at *ca.* 27 °C. The white residue was collected on a glass filter, washed with ether, and dried *in vacuo*. Yield: 74 %.

*(2,2′-Bipyridine)(3-hydroxy-2-methyl-4-pyronato)palladium(II) 3-Hydroxy-2-methyl-4-pyronate, [PdL(bpy)]L (**4a**):* To a stirred suspension of Compound **1** (3 mmol) in chloroform (15 ml) we added a chloroform solution (2 ml) of 2,2′-bipyridine (3 mmol), after which the mixture was stirred for *ca.* 1 h. The yellow precipitate thus obtained was filtered, washed with chloroform and ether, and then dried *in vacuo*. Yield: 76 %. This compound is fairly hygroscopic, and a color change from yellow to reddish yellow occurs in the presence of moisture. By using 1,10-phenanthroline instead of 2,2′-bipyridine, a yellow precipitate of [PdL(phen)]L (**4b**) was also obtained in a 43 % yield. This compound is also hygroscopic, and a change in color to reddish yellow also takes place in the presence of moisture.

Although we could not isolate Compounds **4a** and **4b** in a satisfactory purity, as the analytical data in Table 1 indicate, we obtained stable complex salts, **4c**—**4f**, by replacing the counter ion, L, with a perchlorate or tetraphenylborate anion.

(2,2'-Bipyridine)(3-hydroxy-2-methyl-4-pyronato)palladium(II) Perchlorate, [PdL(bpy)]ClO_4 (4c): To an aqueous ethanol (1: 1 by volume) solution (40 ml) of 2,2'-bipyridine (1.5 mmol) we added Compound **1** (1.5 mmol); then we stirred the mixture for *ca.* 1 h at room temperature. After the removal of the insoluble materials by filtration, an aqueous solution (10 ml) of $NaClO_4$–H_2O (1.5 mmol) was added to the yellow filtrate. The yellow precipitate thus obtained was filtered, washed with water, ethanol, and ether successively, and then dried *in vacuo*. Yield: 73 %. By using $NaB(C_6H_5)_4$ in place of $NaClO_4 \cdot H_2O$, a yellow precipitate of [PdL(bpy)]$B(C_6H_5)_4$ (**4d**) was also obtained in a 71 % yield.

The corresponding 1,10-phenanthroline complexes, [PdL(phen)]ClO_4 (**4e**) and [PdL(phen)]$B(C_6H_5)_4$ (**4f**), were obtained as yellow precipitates by the same methods as were used for Compounds **4c** and **4d** respectively, using 1,10-phenanthroline instead of 2,2'-bipyridine. The yields were 80 and 76 % respectively.

Reactions of [Pd(N)$_4$]L$_2$ (2) and [Pd(NN)$_2$]L$_2 \cdot n$H$_2$O (3) with Sodium Iodide. To an ethanol solution (5 ml) containing Compound **2a** (0.5 mmol) we added an ethanol solution (3 ml) of NaI (1.0 mmol), after which the mixture was stirred for *ca.* 45 min. The red brown precipitate thus obtained, [$PdI_2(pa)_2$], was filtered, washed with ethanol and then ether, and dried *in vacuo*. Yield: 60 %. (Found: C, 14.95; H, 3.84; N, 5.60 %. Calcd for [$PdI_2(pa)_2$]=$C_6H_{18}N_2I_2Pd$: C, 15.06; H, 3.79; N, 5.86 %.) Other compounds, [$PdI_2(ba)_2$], [Pd(en)$_2$]I_2, [Pd(tn)$_2$]I_2, and [Pd(*N*,*N*-Me_2en)$_2$]I_2, were also obtained similarly from the reactions of Compounds **2b**, **3a**, **3b**, and **3c** with NaI, in the mole ratio of one to two in each case. (Found for [$PdI_2(ba)_2$]: C, 29.08; H, 3.13; N, 4.90 %. Calcd for $C_{14}H_{18}N_2I_2Pd$: C, 29.27; H, 3.16; N, 4.88 %. Found for [Pd(en)$_2$]I_2: C, 10.41; H, 3.45; N, 11.72 %. Calcd for $C_4H_{16}N_4I_2Pd$: C, 10.00; H, 3.36; N, 11.66 %. Found for [Pd(tn)$_2$]I_2: C, 14.19; H, 4.08; N, 10.84 %. Calcd for $C_6H_{20}N_4I_2Pd$: C, 14.17; H, 3.96; N, 11.02 %. Found for [Pd(*N*,*N*-Me_2en)$_2$]I_2: C, 17.92; H, 4.52; N, 10.39 %. Calcd for $C_8H_{24}N_4I_2Pd$: C, 17.91; H, 4.51; N, 10.44 %.)

Reaction of [PdL(bpy or phen)]L with Lithium Bromide and Sodium Iodide. An ethanol solution (10 ml) of LiBr–H_2O (15 mmol) was stirred into a yellow aqueous ethanol solution (1: 3 by volume) of [PdL(bpy)]L (1.5 mmol) *in situ*. After the stirring had continued for *ca.* 40 min, the yellowish brown precipitate thus obtained was filtered, washed with ethanol and ether, and then *in vacuo*. Yield: 70 %. (Found: C, 28.42; H, 1.89; N, 6.43 %. Calcd for [$PdBr_2$(bpy)]=$C_{10}H_8N_2Br_2Pd$: C, 28.44; H, 1.91; N, 6.63 %.) By using phen instead of bpy, a yellowish brown precipitate of [$PdBr_2$(phen)] was obtained in an 82 % yield (Found: C, 33.29; H, 1.98; N, 6.03 %. Calcd for [$PdBr_2$(phen)]=$C_{12}H_8N_2Br_2Pd$: C, 32.29; H, 1.81; N, 6.28 %.). The corresponding iodo complexes, [PdI_2(bpy)] and [PdI_2(phen)], were also obtained similarly as red brown precipitates from the reactions of [PdL(bpy or phen)]L with twice as many moles of NaI (Found: C, 23.92; H, 1.75; N, 5.32 %. Calcd for [PdI_2(bpy)]=$C_{10}H_8N_2I_2Pd$: C, 23.26; H, 1.56; N, 5.42 %. and Found: C, 27.49; H, 1.56; N, 5.18 %. Calcd for [PdI_2(phen)]=$C_{12}H_8N_2I_2Pd$: C, 26.67; H, 1.49; N, 5.18 %.).

Measurements. The IR spectra in the 200—4000 cm^{-1} region were recorded on a JASCO DS-701G infrared spectrophotometer in Nujol mulls between CsI plates. The PMR spectra were obtained with a JEOL JNM-PS-100 spectrometer. The water contents in the hydrated complexes were determined from the thermogravimetric curves, which had themselves been obtained with a Shimadzu TGA-30 thermobalance at a heating rate of 5 °C/min in an atmosphere of nitrogen flowing at 50 ml/min. The electric conductivities of the solutions were measured with a Toa Electronics CM-2A conductivity meter. The molecular weight was determined with a Hitachi Perkin-Elmer 115-type vapor-pressure osmometer, employing benzil as the reference substance.

Results and Discussion

Bis(3-hydroxy-2-methyl-4-pyronato)palladium(II), [PdL_2] (**1**), reacts with an excess amount of an aliphatic amine to give a complex of the [Pd(N)$_4$]L$_2$ type (**2**) (where N is propylamine (pa) (**2a**) or benzylamine (ba) (**2b**)) or the [Pd(NN)$_2$]L$_2 \cdot n$H$_2$O type (**3**) (where NN is ethylenediamine (en) (**3a**), trimethylenediamine (tn) (**3b**), or *N*,*N*-dimethylethylenediamine(*N*,*N*-Me_2en) (**3c**)). These Pd(II) amine complexes contain the 3-hydroxy-2-methyl-4-pyronate ion as counter anions. When Compounds **2a** and **2b**, which have monodentate amines, were reacted with twice as many moles of NaI, two of the coordinated amines were replaced by two iodide anions to afford neutral complexes, [$PdI_2(pa)_2$] and [$PdI_2(ba)_2$] respectively. On the other hand, when Compounds **3a**, **3b**, and **3c**, which have bidentate amines, were treated with twice as many moles of NaI, the 3-hydroxy-2-methyl-4-pyronate ions were replaced by iodide anions to give [Pd(en)$_2$]I_2, [Pd(tn)$_2$]I_2, and [Pd(*N*,*N*-Me_2en)$_2$]I_2 respectively.

The parent complex, Complex **1**, reacts with an equimolar amount of a heterocyclic nitrogen base such as bpy and phen to give rise to [PdL(bpy or phen)]L, (**4a**, **4b**). Even when twice as many or more moles of bpy or phen were used, a complex of the [Pd(NN)$_2$]L$_2$ type was not afforded, but **4a** or **4b** resulted. Although Compounds **4a** and **4b** could not be isolated in a satisfactory purity, their PMR spectra in the intact solutions indicate unequivocally that two kinds of L exist, one in the coordination sphere and the other in the outer sphere (Table 2). By replacing the counter ion, L, with perchlorate and tetraphenylborate anions, stable complex salts, **4c**—**4f**, were obtained. When the ethanol solutions of **4a** and **4b** *in situ* were treated with an excess amount of LiBr$\cdot$$H_2O$ or twice as many moles of NaI, the coordinated 3-hydroxy-2-methyl-4-pyronate ligand was replaced by two bromide or iodide ions to give [PdX_2(bpy or phen)], where X is Br or I. The analytical and IR data of the newly isolated compounds are listed in Tables 1 and 3 respectively.

[PdL$_2$] (1). Compound **1** exhibits strong IR bands at 1600, 1564, and 1545 cm^{-1}; the former band can be assinged to the C=O, and the latter two, to the C=C stretching vibrations, by reference to the data of the other metal complexes of 3-hydroxy-2-methyl-4-pyrone.[1] The band observed at 419 cm^{-1} can tentatively be assigned to the Pd–O stretching vibration by reference to the data of the bis(acetylacetonato)palladium(II).[7]

In the PMR spectrum of Compound **1** in $CDCl_3$, the signal of the 5-position proton is composed of two doublets, the area ratio of which is 1: 1, as is listed in

TABLE 1. COLOR AND ANALYTICAL DATA OF THE PALLADIUM(II) COMPLEXES

Complex		Color	Found (Calcd), %			
			C	H	N	H_2O
1	$[PdL_2]$	brown	40.26 (40.42)	2.90 (2.83)		
2a	$[Pd(pa)_4]L_2$	white	48.44 (48.61)	7.92 (7.82)	9.33 (9.45)	
2b	$[Pd(ba)_4]L_2$	white	61.41 (61.18)	6.15 (5.91)	6.99 (7.14)	
3a	$[Pd(en)_2]L_2 \cdot 2H_2O$	white	37.52 (37.47)	5.99 (5.90)	10.83 (10.92)	6.78 (7.03)
3b	$[Pd(tn)_2]L_2 \cdot 2.5H_2O$	white	39.01 (39.32)	6.67 (6.42)	10.61 (10.19)	7.43 (8.19)
3c	$[Pd(N,N\text{-}Me_2en)_2]L_2 \cdot 4H_2O$	white	39.80 (39.71)	7.16 (7.00)	9.15 (9.26)	11.69 (11.91)
4a	[PdL(bpy)]L	yellow	47.33 (51.53)	3.23 (3.54)	4.87 (5.46)	
4b	[PdL(phen)]L	yellow	51.11 (53.70)	3.31 (3.37)	4.87 (5.22)	
4c	$[PdL(bpy)]ClO_4$	yellow	38.91 (39.45)	2.68 (2.69)	5.67 (5.75)	
4d	$[PdL(bpy)]B(C_6H_5)_4$	yellow	67.90 (67.96)	4.68 (4.71)	3.83 (3.96)	
4e	$[PdL(phen)]ClO_4$	yellow	42.03 (42.29)	2.49 (2.56)	5.53 (5.48)	
4f	$[PdL(phen)]B(C_6H_5)_4$	yellow	69.30 (69.01)	4.47 (4.55)	3.85 (3.83)	

TABLE 2. PMR SPECTRA OF THE PALLADIUM(II) COMPLEXES AT ROOM TEMPERATURE

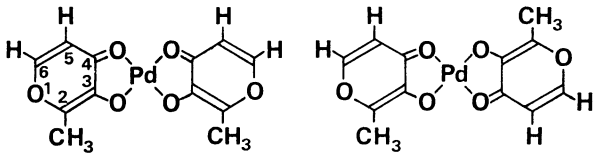
Compound	Solvent	L			Bases
		CH_3	H^5	H^6	
1	$CDCl_3$[a]	2.42 (6H, s)	6.29 (1H, d) 6.52 (1H, d)	7.66 (2H, d)	
2a	$CDCl_3$[a]	2.17 (6H, s)	6.11 (2H, d)	7.44 (2H, d)	0.79 (12H, t, $-C\underline{H}_3$), 1.48 (8H, unresolved sex, $-CH_2-C\underline{H}_2-CH_3$), 2.62 (8H, broad, $-C\underline{H}_2-NH_2$), 5.80—6.40 (8H, $-N\underline{H}_2$)[c]
	D_2O[b]	2.75 (6H, s)	6.78 (2H, d)	8.23 (2H, d)	1.36 (12H, t, $-C\underline{H}_3$), 2.09 (8H, sex, $-CH_2-C\underline{H}_2-CH_3$), 3.04 (8H, t, $-C\underline{H}_2-NH_2$)
2b	$CDCl_3$[a]	1.20 (6H, s)	5.74 (2H, d)	d)	3.78 (8H, broad, $-C\underline{H}_2-NH_2$), 6.70—7.80 (m, $\underline{H}^6$, $-CH_2-N\underline{H}_2$ and $-CH_2-$)
3a	D_2O[b]	2.73 (6H, s)	6.75 (2H, d)	8.20 (2H, d)	3.10 (8H, s, $-C\underline{H}_2-NH_2$)
3b	D_2O[b]	2.75 (6H, s)	6.78 (2H, d)	8.24 (2H, d)	2.14 (4H, quin, $-CH_2-C\underline{H}_2-CH_2-$), 3.08 (8H, t, $-C\underline{H}_2-NH_2$)
3c	D_2O[b]	2.69 (6H, s)	6.72 (2H, d)	8.20 (2H, d)	3.05 (s, $-N-(C\underline{H}_3)_2$, 3.04—3.20 (m, $-C\underline{H}_2-N-(CH_3)_2$),[e] 3.20—3.28 (4H, m, $-C\underline{H}_2-NH_2$)
4a	D_2O[b]	2.52 (3H, s) 2.80 (3H, s)	6.76 (1H, d) 6.87 (1H, d)	f)	7.70—8.70 (m, $\underline{H}^6$ and bpy)
4b	D_2O[b]	2.22 (3H, s) 2.70 (3H, s)	6.31 (1H, d) 6.75 (1H, d)	g)	7.20—8.80 (m, $\underline{H}^6$ and phen)
4c	$(CD_3)_2SO$[a]	2.20 (3H, s)	6.53 (1H, d)	f)	7.50—8.40 (9H, m, $\underline{H}^6$ and bpy)

a) TMS was used as an internal reference. b) TMS was used as an external reference. c) The signal overlaps with 5-position proton of the pyronate anion, the composite area corresponding to 10H. d) The signal overlaps with the amine and phenyl protons of ba. e) The signal overlaps with the methyl protons of the N,N-Me_2en, the composite area corresponding to 16H. f) The signal overlaps with the bpy resonances. g) The signal overlaps with the phen resonances.

TABLE 3. CHARACTERISTIC IR BANDS (cm^{-1}) OF THE PALLADIUM(II) COMPLEXES

Compound	ν (C=O)	ν (C=C)			ν (M–O)	ν (M–N)	δ (N–M–N)	Others			
1	1600	1564	1545		419						
2a	1612	1573	1514								
2b	1612	1573	1516								
3a	1607	1595	1552			520	288				
3b	1604	1559	1499			512	257				
3c	1603	1567—1558		1510		510	269				
4c	1594	1564	1543		411			768	722	1110—1075	622
4d	1604	1565	1550		411			764	720		
4e	1596	1564	1550		410			1632	1520	1090—1074	622
4f	1598	1566	1548		410			1633	1520		

Table 2. The spectral pattern suggests the coexistence of two different magnetic environments for the 5-position protons. The complex may exist as a mixture of *cis* and *trans* isomers, as is shown below:



cis *trans*

Whether the two carbonyl groups occupy mutually *cis* or *trans* positions seems to exert a different influence on the proton in question. The nearly equal intensities of the two signals at 6.29 and 6.52 ppm indicate that the *cis* and the *trans* isomers exist in equal amounts in chloroform, although the signal assignments to the two isomers are not possible. The methyl protons and the 6-position protons resonate as a singlet and a doublet respectively. Their insensitivity to the geometrical structure might arise from the fact that they are farther from the donor atoms than the 5-position protons.

Table 4. Molar conductivities of the palladium(II) complexes[a)]

Complex	Solvent	Λ_M
2a	H_2O	119
	EtOH	16.4
2b	EtOH	17.3
3a	H_2O	165
3b	H_2O	163
3c	H_2O	165
4c	DMSO	28.9
4e	DMSO	17.3
$[Pd(pa)_2I_2]$	DMSO	0
$[Pd(ba)_2I_2]$	DMSO	0
$[Pd(en)_2]I_2$	DMSO	95.2
$[Pd(tn)_2]I_2$	DMSO	135
$[Pd(N,N\text{-}Me_2en)_2]I_2$	DMSO	133
$[Pd(bpy)I_2]$	DMSO	4.2
$[Pd(phen)I_2]$	DMSO	8.7

a) Molar conductivity of the 10^{-3} M solution at 25 °C ($ohm^{-1}\cdot cm^2\cdot mol^{-1}$).

$[Pd(N)_4]L_2$ (2). As may be seen in Table 3, these complexes exhibit the ν(C=O) and ν(C=C) bands at 1612 cm^{-1}, and at 1573 and 1515 cm^{-1}, respectively. The ν(C=O) frequency is slightly higher than that for **1**, but it is not diagnostic for the presence of L in the outer sphere. On the other hand, no band is observed in the Pd–O stretching region (400—500 cm^{-1}), suggesting that the 3-hydroxy-2-methyl-4-pyronate anion is not coordinated to the Pd(II) ion. The molar conductivity data (Table 4) indicate that Compound **2a** is a 1:2 electrolyte in water, while Compounds **2a** and **2b** do not dissociate completely in ethanol.[8)] The molecular-weight data of these complexes (Table 5) also show that they are partially dissociated in ethanol. During the measurements of the conductivity and the molecular

Table 5. Molecular-weight data for the $[Pd(N)_4]L_2$ complexes[a)]

Compound	Solvent	Temp °C	Concentration ($\times 10^{-3}$ M)	Calcd	Found
2a	EtOH	40	1.33	593	342
	EtOH	40	3.32		401
	EtOH	40	4.65		435
	$CHCl_3$	30	1.70		606[b)]
2b	EtOH	40	2.51	758	367
	$CHCl_3$	30	2.53		256[c)]

a) The molecular-weight values listed were determined *ca.* 30 min after dissolution. b) This value changed with the time, reaching 538 and 399 *ca.* 1 and 25 h after dissolution respectively. c) This value changed with the time, reaching 240 *ca.* 25 h after dissolution.

weight in ethanol, the color of the solution gradually changed from faintly yellow to yellow orange. These results seem to be caused by ionization and the following ligand substitution:

$$[Pd(N)_4]L_2 \rightleftharpoons [PdL(N)_2]L + 2N \quad (1)$$

The molecular weight of **2a**, determined *ca.* 30 min after dissolution in chloroform, nearly coincides with the calculated value, reflecting poor ionization in this solvent, but the value diminishes with time, suggesting the gradual progress of the ligand substitution of **2a** according to Eq. 1.

In the PMR spectrum of **2a** in D_2O, the signals of the methyl, 5-position, and 6-position protons of 3-hydroxy-2-methyl-4-pyronate anion were observed at 2.75 s, 6.78 d ($J_{5,6}$=5.2 Hz), and 8.23 d ppm respectively. These values coincide with those for the protons of L in $[Pd(NN)_2]L_2\cdot nH_2O$ (**3**), which are 1:2 electrolytes in D_2O, suggesting again that **2a** dissociates completely in D_2O.

On the other hand, Table 5 shows that **2a** exists as the ion aggregate for at least 30 min after dissolution in chloroform; thereafter the substitution and decomposition occur gradually with time. Compound **2b** changes more rapidly in chloroform than does **2a**. The PMR data for **2a** and **2b** in chloroform (Table 2) were taken immediately after dissolution. The protons of L in **2b** resonate at a much higher field than these in **2a**. The benzylamine molecules in the coordination sphere may exert an anisotropic magnetic effect on L in the outer sphere.

Recently, Okeya *et al.*[9)] found that hydrogen exchange occurs between $CDCl_3$ and amine protons in palladium(II) amine complexes containing a β-diketonate anion in the outer sphere, $[PdL_4](\beta\text{-dik})_2$ and $[Pd(\beta\text{-dik})L'_2](\beta\text{-dik})$, where L=primary amine, L'=secondary amine, and β-dikH=acetylacetone or trifluoroacetylacetone. In the present PMR studies of **2a** and **2b** in $CDCl_3$, the hydrogen-exchange reactions between $CDCl_3$ and propylamine and benzylamine are also observed, the signal due to the amine proton diminishing and the peak due to $CHCl_3$ growing concurrently with time (Fig. 1). The pK_a value of HL (8.61)[10)] is near that of acetylacetone (8.82),[10)] and the pyronate anion, L, in

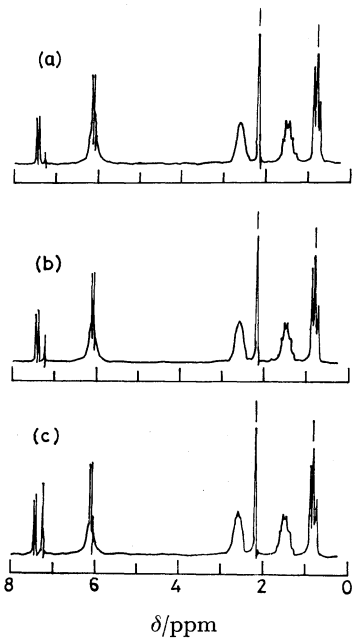


Fig. 1. The PMR spectra of $[Pd(pa)_4]L_2$ [**2a**] in $CDCl_3$ 5 min (a), 30 min (b) and 100 min (c) after dissolution, respectively.

the outer sphere may accept a hydrogen ion from the amine in the coordination sphere:

$$[Pd(RNH_2)_4]^{2+}(L^-)_2 \rightleftarrows [Pd(RNH)(RNH_2)_3]^+L^-(HL) \quad (2)$$

$$[Pd(RNH)(RNH_2)_3]^+L^-(HL) + CDCl_3 \longrightarrow [Pd(RNHD)(RNH_2)_3]^{2+}(L^-)_2 + CHCl_3 \quad (3)$$

$[Pd(NN)_2]L_2 \cdot nH_2O$ (3). The water contents of **3a**, **3b**, and **3c** were determined from the thermogravimetric curves of these complexes. The TG curves show that the liberation of the water occurs at around 45—110 °C in either case. In the IR spectra of the dehydrated complexes, the intensity of the fairly strong and broad bands which appeared at 3170 (**3a**), at 3460 and 3340 (**3b**), and at 3325 and 3180 (**3c**) cm^{-1}, diminished, although none of these bands except the 3460 and 3340 cm^{-1} bands disappeared completely. These results suggest that the bands observed in the 3170—3460 cm^{-1} region are mainly due to the O–H stretching vibration, although the NH_2 stretching bands also appear in this region. These complexes exhibit no band in the Pd–O stretching region, but they do show the Pd–N stretching and N–Pd–N bending bands, suggesting that L is contained in the outer sphere, as in the cases of **2a** and **2b**. The tentative assignment of the ν(Pd–N) and δ(N–Pd–N) bands is based on the data for $[Pd(en)_2]X_2$ (where X=Cl, Br, or I).[11] The molar conductivity data of these complexes also indicate that all three complexes are 1:2 electrolytes in water.

In the PMR spectra of these complexes in D_2O, the signals due to the methyl, 5-position, and 6-position protons of the 3-hydroxy-2-methyl-4-pyronate anion were observed at about 2.72 s, 6.75 d, and 8.22 d ppm respectively, as is shown in Table 2. Although *cis* and *trans* isomers are possible for Compound **3c**, the methyl and methylene $-C\underline{H}_2-NH_2$ protons of *N,N*-dimethylethylenediamine appear as a kind of singlet and a kind of multiplet at 3.05 and 3.26 ppm respectively, while the methylene $-C\underline{H}_2-N-(CH_3)_2$ protons overlap with the methyl protons of *N,N*-Me_2en. This spectral behavior seems to suggest that **3c** exists in D_2O solely as the *trans* or *cis* isomer or that, alternatively, the two isomers exhibit identical chemical shifts by chance.

The counter anion, L, in $[Pd(NN)_2]L_2 \cdot nH_2O$ (**3**) can readily be replaced by treating it with double the molar amount of sodium iodide in ethanol to precipitate the $[Pd(NN)_2]I_2$ complex in a 75—85% yield. This behavior is contrasted with that of the unidentate-amine complex, Complex **2**, which readily reacts with sodium iodide in ethanol to precipitate $[PdI_2(N)_2]$. The bidentate-amine in **3** is bonded to Pd(II) much more strongly than is the unidentate-amine in **2** and resists being displaced by the iodide ion.

$[PdL(bpy\ or\ phen)]X$ ($X=ClO_4$ or $B(C_6H_5)_4$) (4). The infrared data of these complexes suggest that: (a) The perchlorate ion is not coordinated to the palladium ion, since the bands at 1070—1110 *vs.* and 622 cm^{-1} assigned to the perchlorate ion are not split in Compounds **4c** and **4e**. (b) The bpy ligand is coordinated to the palladium ion, since the characteristic band (751 cm^{-1}) of the free bpy is shifted and split to 765 and 720 cm^{-1} in **4c** and **4d**.[12] (c) The phen ligand is coordinated to the palladium ion, since the characteristic bands (1505 and 1605 cm^{-1}) of the free phen are shifted to 1520 and 1632 cm^{-1} respectively in **4e** and **4f**.[13] (d) The 3-hydroxy-2-methyl-4-pyronate anion is coordinated to the palladium ion, since the band (410 cm^{-1}) assignable to the Pd–O stretching vibration is observed for all the complexes, **4c**, **4d**, **4e**, and **4f**. The molar conductivity data of **4c** and **4e** indicate that these complexes are 1:1 electrolytes in dimethyl sulfoxide,[8] supporting the idea that the perchlorate ion is not coordinated to the palladium ion. Compounds **4d** and **4f** are not soluble in common solvents and prevent any conductivity measurement. In the PMR spectrum of **4c** in $(CD_3)_2SO$, the signals of the methyl protons and the 5-position proton of the pyronate ligand were observed at 2.20 s and 6.53 d ppm ($J_{5,6}=5.2$ Hz) respectively, but no signal of the 6-position proton is discernible because of overlapping with the bpy resonances. The appearance of one kind of doublet due to the 5-position proton is in accordance with the lack of geometrical isomers for this complex, contrary to the coexistence of the *cis*- and *trans*-$[PdL_2]$ isomers in the $CDCl_3$ solution. Unfortunately, **4e**, like **4d** and **4f**, is not soluble enough in common solvents to give PMR spectra.

The authors would like to thank Miss Yoshimi Murooka and Miss Keiko Fujita for their experimental assistance. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

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